A TEXT BOOK OF
THEORETICAL & INORGANIC
CHEMISTRY

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NEW REVISED EDITION

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PART I

HISTORICAL INTRODUCTION

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THE Object and chief End of Chymistry,' wrote PIERRE JOSEPH MACQUER (1718–84), ' is to separate the different substances that enter into the composition of bodies; to examine each of them apart; to discover their properties and relations; to decompose those very substances, if possible; to compare them together, and combine them with others; to reunite them again into one body so as to reproduce the original compound with all its properties; or even to produce new compounds that never existed among the works of Nature.' Though these words were written nearly two centuries ago, it would be difficult to frame a more lucid or more accurate definition of that most fascinating of all sciences, which has captivated untold numbers of the finest human intelligences and upon which civilization itself ultimately rests.

The story of the origin and development of chemistry is not a subject of mere antiquarian interest. An adequate knowledge of it is an indispensable part of the equipment of any chemist who aspires to make noteworthy advance in chemical discovery or even to master the science as it is to-day. It is a significant fact that, almost without exception, the prominent landmarks on the chemical high road were set up by men deeply versed in the discoveries and ideas of their predecessors. BOYLE, DALTON, PRIESTLEY, LAVOISIER, BERZELIUS, LIEBIG, KEKULÉ, VAN'T HOFF, ARRHENIUS, and RAMSAY—to name only a few of the great geniuses of chemistry—were all serious students of chemical history; and it would be hard to over-estimate the part that this study played in fecundating and maturing their scientific work, whether speculative or practical.

The reason is not far to seek. Chemistry, like other experimental sciences, is of a twofold nature. Before the woof of facts can form a coherent fabric, it must be woven across the warp of theory; both are necessary and each is dependent on the other. There have been periods in the history of chemistry when theory and practice were widely divorced, and in such periods practice has degenerated into an empirical craft while theory has become a barren philosophy. At the present time, new chemical facts appear in myriads every year. Any man or woman of reasonably good

intelligence can be trained in a few years to carry out original research; the journals of learned societies distend ominously, and the archives suffocate with the press of unpublished, though doubtless meritorious, communications.   Facts in themselves—however numerous, however well authenticated, however well known— may have little or no importance.   The increase in weight that metals undergo on calcination was known for many hundreds of years before LAVOISIER made it a lever with which to overthrow the whole theoretical structure of eighteenth-century chemistry. CAVENDISH'S observation that a minute fraction of atmospheric nitrogen could not be made to combine with oxygen under the influence of the electric spark remained an isolated and therefore unimportant fact for over a century.   Facts become important when integrated into some comprehensive scheme, when informed by some far-reaching theory, when set harmoniously in the structure of some broad concept; since thus the way is prepared for a great stride in advance—a stride that could never have been achieved by the mere chaotic collection of facts *qua* facts.

The ability to perceive a fundamental connection between facts that are apparently unrelated is, in its highly-developed form, a mark of genius.   To some extent, however, it is common to all of us, and it is an ability that may be trained and cultivated. Entirely original ideas arise much less frequently than is sometimes supposed, in science as in other departments of human intellectual activity.   Though they are now applied to very different matters, many of the ideas at present current in chemistry may be closely paralleled in the Neoplatonist natural philosophy of fifteen or sixteen centuries ago, while the views of certain modern physicists on the ultimate nature of the universe could have been accepted by PLATO himself without serious violence to his philosophical scheme.

The principal value of a study of the history of chemistry lies in the familiarity it gives us with the speculative reflections of great chemists of the past.   Such men as BOYLE were the intellectual peers of our most celebrated contemporary chemists, and though the facts with which they were acquainted were immeasurably fewer than those that fill the pages of MELLOR and BEILSTEIN, their insight into the natural world has been a perennial source of inspiration to later workers.   In the long course of man's effort to interpret, and in some measure to control, the phenomena of Nature, ideas have invariably proved a more potent weapon than technical skill.   The chemist, therefore, while perfecting the technique that provides the raw material of his science, will not neglect the invaluable treasury of ideas amassed by his chemical forbears

There is a further reason why an acquaintance with the main course of the history of chemistry is not merely a desirable, but an essential, attribute of the properly-equipped chemist. It is simply this: that a critical appraisal of the present is impossible without a just appreciation of the past. However laudable unquestioning submission to authority may be in the disciple of a revealed religion or in the citizen of a state, it is a serious blemish in the man of science. DALTON'S anathema on GAY-LUSSAC and AVOGADRO delayed the progress of chemistry by nearly half a century. 'Thou canst not split an atom' became a dogma, and dogma cannot be tolerated in science. Science can avoid sterility only if it is recognized that scientific theory is always provisional but never final. The surest way for a chemist to arrive at an understanding of the theories he wields to-day is to trace their development step by step, and to profit by the spectacle of discarded theories whose bones lie bleaching by the roadside.

The following sketch of the history of chemistry is designed to throw into relief the principal episodes of that history, in order that the remaining parts of the book may be seen in their true perspective. If it fulfils its purpose, it will reveal present-day chemistry as the latest phase of a dynamic process, whose origin was coeval with the birth of civilization and whose end no man can foresee.

The Main Periods of Chemical History.

While sharp delimitation is both impossible and undesirable, it is convenient to regard the development of chemistry as characterized by five main periods, viz.:

1. *The Empirical Age.*
2. *The Period of Alchemy.*
3. *The Period of Iatrochemistry.*
4. *The Period of Pneumatic Chemistry.*:
5. *The Modern Age, from Lavoisier and Dalton to the present day.*

Each period, however, passes imperceptibly into that which succeeds it, and it is no more possible to give a definite date for the transition than it is to say exactly when a child ceases to be a child and becomes a youth.

THE EMPIRICAL AGE

The Origins of Chemistry.—There can be no doubt that the origins of chemistry are to be found in the technical arts and crafts of primitive civilizations. The extraction of metals from their ores, the manufacture of glass and soap, the arts of painting and

dyeing, the preparation of perfumes, unguents, and cosmetics, the practice of mummification, and similar accomplishments of early civilized man, all imply an extensive acquaintance with the kind of facts on which chemistry is based.   We may therefore reasonably call the sum of such knowledge the ' chemistry ' of those remote ages, and it cannot be denied that the genius who first deliberately extracted copper from malachite is fully entitled to inclusion in the chemical Valhalla.

The question of the origin of civilization is, and is likely to remain, a subject for somewhat acrimonious discussion and considerable further investigation.   Fortunately there is no need for us to enter the lists, since there could be no earlier stage of chemistry than the empirical, and this continued to exist well into the period of written historical record.   The civilizations of the ancient world—Egypt, Sumer and Akkad, Assyria, Babylonia, India, and China — all possessed accomplished craftsmen and artisans, and all doubtless made notable contributions to the stock of empirical chemical knowledge.

Egypt.—We cannot, however, dismiss the matter in quite so summary a fashion, since modern European chemistry has definite affiliation to one of these civilizations, namely that of ancient Egypt.   How much it owes to the others is still conjectural; but the path from Heliopolis to Heidelberg, from Memphis to Manchester, lies like an unbroken thread across the chart of chemical history.   Though our estimates may possibly have to be revised, it seems that the Egyptians were a hard-headed, practical race, more like the Romans than the Greeks, preferring action to reflection, and caring little for those philosophical speculations so dear to classical Athens.   They therefore made no contributions, that we can discover, towards any system of chemical theory.   On the other hand, they raised such chemical industries as metallurgy and glass-making to a degree of efficiency without parallel in later times until the dawn of the modern period; and their skill in metallurgy in particular was the condition and the occasion of the effective birth of chemistry some centuries later.

In Egypt, the comparatively useless but extremely attractive metal gold had already acquired that factitious value which it has retained ever since.   The reasons for this vagary need not concern us—they were very largely of a superstitious nature—but it is hardly an exaggeration to say that chemistry as a science owes its existence to the esteem in which gold was held in the ancient world.   As accomplished metallurgists, the workers in the laboratories attached to the Egyptian temples produced innumerable alloys, some of which closely resembled gold in appearance.   Though the craftsmen were probably far too shrewd to deceive themselves,

it would have been only in accordance with human nature if they sometimes imposed upon others less well informed, passing off as genuine gold what was only a spurious alloy. Whatever the facts of the case, a legend arose to the effect that base metals could be transmuted into gold—and with the diffusion of that legend chemistry ceased to be a mere empirical craft, changing its honest fustian for the glittering robes of a chimerical art. Chemistry, the art of Egypt, or *Khem* (' the Black Land '), became indeed a dark and dubious pursuit.

THE PERIOD OF ALCHEMY

Philosophical Speculation. — Before we can understand the developments that led to the supposed art of gold-making, we must turn for a time to the philosophical speculations of the Greeks. The classical atomic theory will be considered at a later stage (p. 38); our immediate concern is the theory of ARISTOTLE (384–322 B.C.) on the constitution of matter. Aristotle supposed that the basis of the material world was a primitive matter of *prima materia*, which had, however, only a potential existence until impressed with *Form*. Form is that which gives to every body its individuality. In its simplest manifestation it gives rise to the ' Four Elements,' Fire, Air, Water, and Earth, which are distinguished from one another by their *qualities*. The four primary qualities are the fluid, the dry, the hot, and the cold, and each element possesses two of them. Hot and cold, however, and fluid and dry, are contraries and cannot be coupled; hence the four possible combinations of them in pairs are:

> *Hot and dry*, assigned to Fire.
> *Hot and fluid*, assigned to Air.
> *Cold and fluid*, assigned to Water.
> *Cold and dry*, assigned to Earth.

In each element one quality predominates over the other: in Earth, dryness; in Water, cold; in Air, fluidity; and in Fire, heat. None of the four elements is unchangeable; they may pass into one another through the medium of that quality which they possess in common. Thus fire may pass into air through the medium of heat, air into water through the medium of fluidity, and so on. All other substances are composed of *all* the elements, and the proportion in which the various elements occur in different substances is infinitely variable; hence the existence of such an enormous number of distinct compounds. But since each element can, as we have seen, be transformed into any other, it follows that any compound can likewise be transformed into any other by some

device or treatment that will alter the relative proportions between the elements of which it is composed. Here we have the germ of all theories of metallic transmutation. If lead and gold both consist merely of fire, air, water, and earth, all of which are inter-convertible, why may the former metal not be transmuted into the latter? Such was the question with which generation after generation of chemists confounded the sceptics and justified their ceaseless search for the unattainable.

It is a curious fact that similar views on the constitution of matter arose — presumably independently — in China. Even as early as the twelfth century B.C. the Chinese postulated five material principles of natural objects. These five (*Wu-hsing*—' the quintet ') were water, fire, wood, gold, and earth. ' Water is that which soaks and descends; fire is that which blazes and ascends; wood that which is straight and crooked; gold that which obeys and changes; and earth that which is of use for seed-sowing and harvest. That which soaks and descends becomes salt; that which blazes and ascends becomes bitter; that which is crooked and straight becomes sour; that which obeys and changes becomes acrid; and from seed-sowing and harvest comes sweetness.' [1] Later on, perhaps about the fifth or fourth century B.C., the scientific notion of Yin and Yang, or the two contrary principles, appears to have become established in China. According to this philosophy, the entire universe was identical in substance and was animated and dominated by a cosmic soul, manifesting itself in the dual forces of Yin and Yang. Yin originally referred to the obscuration of the sun by clouds, while Yang signified the bright aspect of banners fluttering at sunrise. Soon, however, Yin was regarded as the female element, typifying the more material and undesirable phenomena of Nature, while Yang became the male element, representative of the more spiritual and desirable qualities. All minerals and metals—like every other substance—were supposed to be substantially the same, but differed in properties in proportion to their relative infusion with Yin and Yang. Base metals might therefore be transmuted into precious metals by the dual method of eliminating the more material Yin qualities in their composition, and by augmenting or refining the more spiritual Yang qualities.

In India, speculations of a comparable nature may be found in the ancient writings, and to the best of our knowledge they were indigenous. The philosophy of the time appears to have tended invariably towards an interpretation of the structure of the world in terms of qualities rather than of distinct and discrete material

[1] Davis and Lu Ch'iang Wu, 'Chinese Alchemy,' *Scientific Monthly* (1930), 31, 226.

substances. Could one have questioned a chemist of the fourth century B.C. as to his fundamental convictions of the nature of gold, he would probably have replied that, below or behind the qualities that appeal to the senses, there is an amorphous, plastic, colourless, inchoate ' metallic ' material, upon which, in the case of gold, have been imposed the qualities of yellowness, heaviness, non-corrodibility, and so on. These qualities he would have regarded as independent of one another, so that the yellowness, for instance, might be removed without affecting the others. A different metal, such as copper, would have the same underlying material, but a different set of infused qualities; and so for iron, silver, and the remaining metals.

If we return to ARISTOTLE, we shall find that, as a minor development of his theory of the Four Elements, he put forward a hypothesis that exerted upon the future development of chemistry an influence out of all due proportion to its real value. In his *Meteorologica* he suggested that the immediate constituents of minerals and metals are two ' exhalations,' one an ' earthy smoke ' and the other a ' watery vapour '; the former consists of small particles of earth on the way to becoming fire, while the latter consists of small particles on the way to becoming air. Neither exhalation is ever entirely free from some admixture of the other. Stones and other minerals are formed when the two exhalations become imprisoned in the earth, the dry or smoky exhalation predominating. Metals are formed under similar circumstances if the watery exhalation predominates. In other words, metals and minerals, in common with every substance under the sun, are composed of each of the four elements, but in metals the predominating elements are water and air (chiefly water), while in minerals they are earth and fire (chiefly earth). It is a signal mark of the paucity of human ideas that this naïve hypothesis should have been accepted, in more or less modified forms, until the close of the eighteenth century.

Alexandrian Chemistry.—The foregoing examples suffice to indicate the kind of philosophical views held by educated men shortly before the opening of the Christian Era. It will be observed that they had extremely little relation to observed facts, and that the importance of experiment as a factor in the investigation of Nature was almost entirely unperceived. To the cultured Greeks, manual work of any kind was undignified, if not actually degrading, so that although the scientific habit of mind was by no means lacking, the only sciences in which the Greeks made noteworthy progress were astronomy and mathematics, both at that time non-experimental.

In 332 B.C. Alexander the Great founded the city of Alexandria

which rapidly grew to be the largest and most important town of the ancient world. The Greek colony included some of the most celebrated scholars of the time, notably EUCLID, ARCHIMEDES, HIPPARCHUS, ERATOSTHENES and APOLLONIUS OF PERGA, and a museum or university was built to accommodate the throng of students and professors attracted thither from various parts of Greece. Soon, however, a *fin de siècle* atmosphere began to envelop the intellectual life of the city, and the odd mystical philosophies that frequently characterize such a period sprang up on every hand like rank and noxious weeds. Superstition of the grossest sort, magic, necromancy (not to mention hydromancy, pyromancy, geomancy, oneiromancy and omphalomancy), sapped the intelligence and clouded the vision of the majority of contemporary thinkers. It is true that two of the philosophical schemes, namely Gnosticism and Neoplatonism, contained much to be admired; but all were alike in forming an extremely unhealthy environment for a rational science.

It was, however, in this very environment that theoretical chemistry originated; and it bore the mark of its origin for many a long day. The Greek settlers, themselves ignorant of metallurgy, could only look on with awe at the achievements of the Egyptian craftsmen, and we may readily suppose that they formed a credulous audience for the narrators of the transmutation legend. A yellow alloy that looked like gold would be sufficient to deceive a man unversed in the goldsmith's art; we may remember that as recently as the reign of Queen Elizabeth an expedition brought back shiploads of iron pyrites from Greenland in the belief that the yellow particles were small nuggets of gold. In the absence of any system of qualitative analysis, deceit was less likely to be discovered, and the ancient equivalent of the gold-brick swindle must have been successfully accomplished on countless occasions.

Very typical of the prevailing intellectual background is the fact that the reality of transmutation appears to have been almost universally accepted, with few or no attempts to arrive at a definite conclusion by crucial experiment. What actually happened was very different. Uncritically believing that the base metals might, in all verity, be changed by chemical art into the purest gold, the philosophizers of the time at once began to spin amazingly elaborate webs of theoretical speculation to explain the transmutation. Most of their fanciful hypotheses have been lost; those that remain are for the most part unintelligible, or, if intelligible, then puerile. Yet although they may in themselves be of little value, the fact that men were at last beginning to reflect about phenomena of a definitely chemical character is an indication that the empirical age of chemistry was on the wane, and that theory and practice

were betrothed if not yet married. The desire for wealth stimulated the chemist to ingenious labour, and from the few intelligible treatises of the early centuries of the Christian Era we gather that a wide knowledge of chemicals and chemical reactions had been acquired. ZOSIMUS the Panopolitan, for example, who could be as incomprehensible as any of his contemporaries of the third century A.D., has some lucid passages in which he mentions the preparation of mercury from cinnabar, of arsenic from arsenic sulphide, and of litharge from lead via white lead, together with several other operations of a similar kind. However meanly we may think of their chemical theory, we must admit that among the Alexandrian chemists were many who excelled at the practice of the laboratory.

The Moslem Chemists.—So matters rested until Islam burst upon a startled world in the seventh century A.D. The Moslem Era dates from the year A.D. 622, when the Prophet Mohammed, despised and rejected of his fellow-townsmen of Mecca, fled to Medina, there successfully to pursue his task of welding the heterogeneous tribes of Arabia into a powerful and united nation. Within one hundred and fifty years from the date of the Flight, Islam had subdued by far the greater part of the ancient world, and her armies were but a few days' march from Paris and the shores of the English Channel. Repulsed by CHARLES THE HAMMER at Poitiers, the Moslems retired beyond the Pyrenees, but from Spain they were not dislodged until the close of the fifteenth century.

For some five or six centuries, Islam was the repository of wisdom and the acme of civilization. To the cultured and courtly gentleman SALADIN, RICHARD CŒUR DE LION must have appeared an uncouth though courageous barbarian, imbued with manly virtue but sadly lacking in refinement. In the realm of learning the circumstances were similar; Christian students flocked to Moslem universities, and Greek knowledge reached the West mainly by way of Latin translations of Arabic versions of the Greek originals. The love of learning, so intense in medieval Islam, extended to the doubtful science of Khem, which the Arabs, adding their definite article *al*, called *alkimia*, whence ' alchemy ' and finally the modern *chemistry, chimie,* and *Chemie.*

From the time when they first appeared on the pages of history, until the present day, the Arabs have been characterized by their sceptical spirit. Moslems of other races—Persians, Berbers, and Copts, for example—have not always shared this spirit, but in the early days of Islam the Bedouin freedom from intellectual restraint made its influence felt far and wide. As a result, chemistry was in part released from the enshrouding bonds of Alexandrian syncretic mysticism, and though alchemy, i.e. gold-making by transmutation,

was still the principal object of chemical research, subsidiary issues were much more thoroughly investigated, and an independent science of rational chemistry grew up side by side with its fantastic and overshadowing companion.

Among the chemists of Islam, the outstanding figures were those of JABIR IBN HAYYAN and RAZI, known to Europe as GEBER and RHAZES respectively. In spite of much research, little is yet known of the personality of JABIR, but he lived in the eighth or ninth century and a large number of treatises on a variety of subjects pass under his name. These books have hitherto escaped a full investigation, but in general they are marked by a just realization of the importance of experiment and by the description of large numbers of chemical facts that appear in them for the first time. It is, however, only to his theory of the constitution of metals that we need refer here; for that theory—a direct descendant of the Aristotelian theory of the two exhalations—gave rise in the course of time to the phlogiston theory of combustion.

JABIR accepted the exhalation theory in its main principles, but seems to have regarded it as too indefinite to explain observed facts or to afford a guide to practical methods of transmutation. He therefore modified it in such a fashion as to make it less vague, and the suggestion he advanced survived, with some alterations and additions, until it was absorbed in the attractive but illusory theory of BECHER and STAHL. The two exhalations, JABIR believed, when imprisoned in the bowels of the earth, were not immediately changed into minerals or metals, but underwent an intermediate conversion. The dry or smoky exhalation was converted into sulphur and the watery exhalation into mercury, and it was only by the subsequent combination of sulphur and mercury that metals were formed. The reason of the existence of different varieties of metals is that the sulphur and mercury are not always pure, and that they do not always combine in the same proportions. If they are perfectly pure, and if, also, they combine in the most complete natural equilibrium, then the product is the most perfect of metals, namely gold. Defects in purity or proportion or both result in the formation of silver, lead, tin, iron, or copper, but since these metals are essentially composed of the same constituents as gold, the accidents of combination may be removed by suitable treatment. Such treatment is the object of alchemy.

To the modern chemist it will at once occur that the above theory might easily have been tested by experimental attempts to obtain metals by the combination of sulphur and mercury. He may be quite sure that such an obvious deduction was not overlooked by JABIR, for in one of his books he describes such an experiment and states that the product was merely cinnabar (HgS). From observa-

tions such as this, JABIR was forced to the conclusion that the sulphur and mercury of which he supposed metals to be composed are not the well-known substances that go by these names, but hypothetical substances to which ordinary sulphur and mercury form the closest available approximations. To put it another way, he was led to postulate an abstract or ' ideal ' sulphur and mercury, a type of theoretical device quite legitimate in itself but demanding a cautious attitude on the part of the user. Such abstractions are common enough even in modern chemistry, but the dangers attaching to them are more adequately realized. Thus, though JABIR's hypothetical sulphur is exactly on a par with our ' ideal gas ' or ' perfect semi-permeable membrane,' every chemist appreciates the fact that it would be a waste of time to indulge in the search for either, and knows that they are merely useful contrivances to simplify argument. How far JABIR's abstractions were from sharing this innocuous character the subsequent history of alchemy manifests only too plainly; yet the sulphur-mercury theory of metals represented a distinct advance upon any that had preceded it, and satisfied the intellectual curiosity of many brilliant scientists for a very lengthy period.

RAZI (866–925) was a man of rather less than JABIR's intellectual calibre, but surpassed him in the ordered clarity of his mind. Like PRIESTLEY, he was a born experimenter with a passion for writing, with the result that in his books we have a better picture of the extent of Moslem chemical knowledge of the early tenth century than exists of any earlier or subsequent period. Since, however, this picture depicts mainly the apparatus employed and the chemicals used, we may leave the reader to refer to the textbooks of the history of chemistry if he desires to study it in detail. More relevant to our present purpose is the violent attack on alchemical pretensions made by the celebrated IBN SINA (AVICENNA), who lived from 980 to 1036 or 1037. IBN SINA—philosopher, physician, poet, and statesman—maintained against the alchemists that the yellow solids they produced were merely imitations of gold. They can, he says, produce these imitations with so great a degree of accuracy as to deceive even the shrewdest, but in such alchemical metals the essential nature remains unchanged: they are simply so dominated by induced qualities that errors may be made concerning their real nature. No true change of a metallic species was considered by IBN SINA to be within the bounds of possibility; but he found few to agree with him, and in the end he seems to have been converted by his opponents. His protest was, however, not without avail, for his books were widely read in medieval Europe, and we may be sure that the seeds of scepticism he sowed bore fruit in due season.

Medieval Europe.—During the twelfth to fourteenth centuries chemistry was imported bodily from Islam to Latin Christianity. Unfortunately, however, it was the alchemical aspect that received most attention and found the most enthusiastic following. Early Latin treatises on chemistry are almost entirely obsessed by the search for the elixirs, two marvellous catalysts that were to convert the base metals first into silver and then into gold. Even such enlightened spirits as ROGER BACON (1214-92) were not sufficiently emancipated to conceive the idea of chemistry simply as a branch of knowledge, and BACON's own canon, *Nothing can be certainly known except by experience*, was by no means equivalent to the canon of science, *Nothing can be certainly known except by experiment.* BACON's 'experience' admittedly included experiment, but it included also intuition and spiritual illumination, so that his position was radically different from the rationalistic attitude of modern science.

The theories by which the alchemists endeavoured to order their indefatigable investigations must not unduly delay us, for, though they served to maintain experimental ardour, they were far more of a hindrance than a help in every other way. Particularly by attracting the foolish, the dishonest, and the incapable to the pursuit of transmutation, alchemy became the object of contempt and suspicion on the part of educated and clear-thinking men. CHAUCER's derisive satire on alchemists in the *Tale of the Chanoun's Yeoman* was thoroughly deserved, while the *Ordinall of Alkimy*, written by THOMAS NORTON of Bristol in 1477, is typical of medieval alchemical literature in describing erroneous facts in ambiguous language. That metals grow in the earth like potatoes; that lead and tin are merely ' unripe ' gold; that gold produces seed which, if sown in mercury or some other suitable soil, will give rise to a golden crop; that metals have sexes and by appropriate matrimony may be made to give birth to gold and silver—these and similar ideas are commonplaces of alchemical thought. Later developments were still more remarkable: the elixir was man himself, and transmutation could be effected by means of quintessence of human brains or by the employment of some other natural or artificial human product. Finally, alchemy became completely estranged from the laboratory, and was absorbed by such fraternities as the Brethren of the Rosy Cross. Its further history is a part of the history of man's credulity.

During the alchemical period of the development of chemistry there was, however, much useful discovery, even though this discovery was a mere by-product. Alcohol, nitric acid, sulphuric acid, hydrochloric acid, silver nitrate, mercuric chloride, and many other essential chemicals, were first prepared and investigated by

the alchemists. Such operations as calcination, distillation, sublimation, crystallization, filtration, and reduction were carefully elaborated and described, and the construction of apparatus received due attention. The application of chemistry to the arts was not neglected, and primitive chemical industries began to make their appearance. The facts necessary for future progress were at length available, and when the time was propitious Nature as usual bore the man who was to provide the requisite stimulus. His name was PARACELSUS.

THE PERIOD OF IATROCHEMISTRY

Paracelsus.—The stimulus applied to chemists by PARACELSUS (1493–1541) was both rude and sharp. A man of extraordinary ability and equally extraordinary behaviour, PARACELSUS' chief characteristic was a supreme contempt for authority. Having become town physician to the city of Basel—through a curious chain of circumstances—he made a bonfire of the medical and alchemical textbooks then popular and proclaimed his own scientific views in arresting, if bombastic, tones. Though he did not deny the possibility of transmutation, and had the most bizarre opinions on the relation between alchemy and the microcosm, he maintained that the search for alchemical gold should not be the chief end of alchemy. Chemists, he averred—and by chemists he was careful to say he meant men who knew the discipline of the laboratory, not those who sat in their studies dreaming the dreams of mystical transmutations—should devote their main energies to the production and purification of drugs for the alleviation of human suffering. He saw that the possibilities of chemo-therapy were unlimited, and called upon his fellows to leave their nauseous old-wives' brews for the remedies that a properly orientated chemistry could provide. In spite of his disagreeable personality his appeal was a success, and the period of iatrochemistry, or medical chemistry, was inaugurated.

The importance of this revolution was twofold. In the first place it diverted the energies of the more reasonable chemists into a saner channel, and in the second place it encouraged physicians to undertake the study of chemistry. Chemistry soon became a necessary part of the education of a medical student, and began to be taught in colleges and medical schools. Alchemy was by no means extinguished; indeed it reached the zenith of its popularity in the century and a half after the death of PARACELSUS—but it continued to attract fewer and fewer of the best minds, and was gradually recognized to be a mischievous delusion.

Iatrochemistry was fertile in the discovery of new substances and new methods, but as barren as alchemy in matters of theory. PARACELSUS himself believed that the universe as a whole and all the objects in it were endowed with life, and that material substances, while ultimately composed of the four Aristotelian elements, are immediately made up of three primary bodies ('hypostatical principles'), viz. *salt*, *sulphur*, and *mercury*—corresponding to *body*, *spirit*, and *soul*. As with the sulphur and mercury of the Moslem alchemists, these primary bodies are merely abstractions of qualities, and their principal merit is that their inadequacy later on provoked the great BOYLE to write his masterpiece, *The Sceptical Chymist*.

The principal iatrochemists, after PARACELSUS himself, were LIBAVIUS (1540–1616), VAN HELMONT (1577–1644), and NICOLAS LÉMERY (1645–1715).

All three of these men made useful contributions to practical chemistry, while LIBAVIUS and LÉMERY are noteworthy for their reasonable scientific outlook, from which the taint of the occult was largely absent. LÉMERY'S great textbook—the *Cours de Chymie*—is a plain and straightforward account of the preparation and properties of substances, much on the lines of a modern treatise; while the theories it contains are definitely attempts to explain observed facts on rational grounds. PARACELSUS' spirit of liberation had now achieved victory, and chemistry was soon to become as free from subservience to medicine as he had taught it to be from alchemy.

The Period of Pneumatic Chemistry

The Scientific Age.—Contemporaneous with VAN HELMONT was GALILEO GALILEI (1564–1642), the man who above all others created the modern world. When GALILEO turned his newly-constructed telescope towards the moons of Jupiter, he altered the whole course of history, for the observations he made enabled the human intelligence to overthrow the stifling burden of scholastic philosophy and to eject ecclesiastical authority from the autocratic control it had hitherto possessed over the faculty of reason. Among the sciences, physics was the first to benefit by the triumph of astronomy, but chemistry was not long in falling into line. In the year of GALILEO's death, ROBERT BOYLE (1627–91) was a boy of fifteen, dabbling with chemicals in a Dorset village. A dozen years later the Warden of Wadham invited him to Oxford, and the future of chemistry was assured.

Robert Boyle.—BOYLE'S work on gases is too well known to need

more than a brief mention.   He perfected the air-pump previously invented by von Guericke, confirmed and extended Torricelli's experiments on atmospheric pressure, and discovered the celebrated law that passes under his name.   We shall see shortly that these advances in gas technique had considerable influence upon subsequent progress in chemistry, but for the moment we must turn to Boyle's demolition of the Aristotelian elements and the Paracelsan hypostatical principles.   In *The Sceptical Chymist* (1661) he asks what real evidence there is that such principles or elements exist, and what reasons there are for supposing that, even if they do exist, they form the common constituents of material objects.   It is true that when a piece of dry wood is burned, fire, water, smoke (or air), and ash (earth) are produced, but he points out (*a*) that there are no grounds for supposing that these substances were present in the wood before combustion, and (*b*) that there is no evidence whatever that the fire, water, smoke, and ash are not themselves complex substances.   He continues as follows:

' Since, in the first place, it may justly be doubted whether or no the fire be, as chymists suppose it, the genuine and universal resolver of mixt compound bodies;

' Since we may doubt, in the next place, whether or no all the distinct substances that may be obtained from a mixt body by the fire were pre-existent there in the formes in which they were separated from it;

' Since also, though we should grant the substances separable from mixt bodies by the fire to have been their component ingredients, yet the number of such substances does not appear the same in all mixt bodies; some of them being resoluble into more differing substances than three; and others not being resoluble into so many as three;

' And since, lastly, those very substances that are thus separated are not for the most part pure elementary bodies, but new kinds of mixts;

' Since, I say, these things are so, I hope you will allow me to inferr, that the vulgar experiments (I might perchance have added, the arguments too) wont to be alledged by chymists to prove, that their three hypostatical principles do adequately compose all mixt bodies, are not so demonstrative as to induce a wary person to acquiesce in their doctrine which, till they explain and prove it better, will by its perplexing darkness be more apt to puzzle than satisfy considering men, and will to them appear incumbered with no small difficulties.'

Boyle then suggests that there is no cogent reason for assigning any arbitrary limit to the number of elements; a more reasonable course, he maintains, is to conduct experiments to try to *discover*

how many there are. The contrast between this attitude and that adopted by earlier chemists is complete; the influence of GALILEO was beginning to make itself felt throughout the body scientific, and the authority of ARISTOTLE was rapidly diminishing almost to vanishing-point. BOYLE is, however, not content with mere destructive criticism; he immediately proceeds to define his own view of an 'element' as it should be conceived in chemistry:

'I mean by elements, as those chymists that speak plainest do by their Principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved. . . . I must not look upon any body as a true principle or element, which is not perfectly homogeneous, but is further resolvable into any number of distinct substances.'

The reader will here recognize our own definition of an element, expressed in the language of the seventeenth century. Except for the fact that the atoms of elements can, by certain physical processes, be split up into electrically charged particles, the definition as it left BOYLE's hands has remained unchanged to the present day.

The Theory of Phlogiston.—Though BOYLE's destruction of the peripatetic 'elements' and the substitution for them of experimentally discoverable elements was of more fundamental importance than his work on gases, it was the latter that exerted the more immediate effect upon the progress of chemistry. The rank and file of the chemical army were not yet mentally prepared for such a revolution as the acceptance of BOYLE's views would have entailed. On the other hand, the spirit of inquiry and experiment was vigorous, so that the new possibility of investigating those wild, aëriform bodies, hitherto untamable and elusive, attracted the attention of many skilful experimenters.

At the same time, the Teutonic inner consciousness of BECHER (1635–82) and STAHL (1660–1734) had evolved a theory of combustion that held sway in chemistry for over a century. Basically, it was a development of the old sulphur-mercury theory, and its pedigree may thus be traced back to the Aristotelian exhalations: a remarkable example of the tenacity of ideas. On the sulphur-mercury theory of metals, the combustion of a metal was explained by assuming the loss of its sulphureous constituent. Advancing knowledge soon rendered this primitive suggestion untenable, and the further hypothesis was made that a combustible body owed its 'combustibility' to the presence in it of an oily constituent. Sulphur, from its greasy feel and from its oily appearance when molten, was believed to be 'an oily fatness of the earth'; hence a metal, containing sulphur as an essential constituent, would

necessarily be combustible. The residue left after the calcination or burning of a metal was regarded as composed of the mercurial constituent, contaminated with more or less earthy impurity.

BECHER and, more particularly, his disciple STAHL crystallized this rather amorphous theory into a useful scientific tool, and although it long outlived its usefulness and became an incubus, it must be regarded as the first great theoretical structure of experimental chemistry. According to STAHL, a ' combustible principle,' *phlogiston* (from φλογίζειν, to inflame), is contained in all combustible bodies, and is given up by them on combustion. Phlogiston becomes appreciable to the senses only when it leaves the body with which it was combined, and appears in the form of fire with its accompaniments of light and heat. The richer a substance is in phlogiston, the more easily it may be burnt, and the more ready it will be to give up phlogiston to substances that do not already possess it, or possess it only in small quantity. As for the actual process of combustion, this is merely a liberation of phlogiston from the body which is being burnt.

Now practically all metals may be converted into an ash by means of heat, even though they may not be inflammable in the ordinary sense of the word; the metallic ashes were known as the *calces* of the metals and the process was called *calcination.* According to STAHL, the calcination or burning of a metal was to be explained in the same way as the combustion of any other combustible body, namely by loss of phlogiston. Metals, in short, were to be considered as compound bodies, each composed of two constituents: phlogiston and calx. Different metals naturally have different calces, but the dual composition is common to all metals. Oil, charcoal, fats, etc., which burn away almost completely and leave little residue, are, from that very property, extremely rich in phlogiston. Hence, if a metallic calx is heated with charcoal, for instance, one might expect the charcoal to give up some of its phlogiston to the calx, thus reconverting the latter into the metal. The fact that metallic calces can thus be ' reduced ' to metal by heating with charcoal had, of course, been known for centuries, and at length a reasonable hypothesis was advanced to explain it.

The reader will do well to assimilate the habit of mind of the phlogiston chemists in order that he may gain a clear understanding of the merits of the phlogiston theory, and realize the magnitude of the task undertaken by LAVOISIER when, towards the close of the eighteenth century, he set out to overthrow it. The rise and fall of phlogiston form an object-lesson on the nature of scientific truth and on the provisional character of scientific theories all the more valuable in that the issues are rarely to be found so sharply

defined elsewhere. The following passage is taken from WATSON's *Chemical Essays* (1781), vol. i; it describes the theory so lucidly that it is worthy of close attention.

' Fire enters, in different proportions, into the composition of all vegetables, and animals, and most minerals, and in that condensed, compacted, fixed state, it has been denominated the *Phlogiston*. Of itself in its natural state of uncombined expansion, fire is not exteemed capable of shining, or burning; when chemically conjoined with the other principles of bodies, it is that alone which conceives and continues those motions, by which bodies are made to shine, to burn, to consume away. All bodies are more or less susceptible of combustion, according to the quantity of this principle which enters into their composition, or the degree of force with which it adheres to them. In the act of burning, and, it may very probably be during the fermentation, and putrefaction, and chemical solutions of various bodies, it recovers its fluidity, is expanded and dispersed into the air, or combined anew with such substances as it has an attraction to. Notwithstanding all that perhaps can be said upon the subject, I am sensible the reader will be still ready to ask—*what is phlogiston?* You do not surely expect that chemistry should be able to present you with a handful of phlogiston, separated from an inflammable body; you may just as reasonably demand a handful of magnetism, gravity, or electricity to be extracted from a magnetic, weighty, or electric body; there are powers in nature, which cannot otherwise become the objects of sense, than by the effects they produce, and of this kind is phlogiston. But the following experiments will tend to render this perplexed subject somewhat more clear.

' If you take a piece of *sulphur*, and set it on fire, it will burn entirely away, without leaving any ashes, or yielding any soot. During the burning of the sulphur, a copious vapour, powerfully affecting the organs of sight, and smell, and the action of the lungs, is dispersed. Means have been invented for collecting this vapour, and it is found to be a very strong acid. The acid thus procured from the burning of sulphur, is incapable of being either burned by itself, or of contributing towards the support of fire in other bodies; the sulphur from which it was procured was capable of both; there is a remarkable difference, then, between the acid, procured from the sulphur, and the sulphur itself; the acid cannot be the only constituent part of sulphur, it is evident that something else must have entered into its composition, by which it was rendered capable of combustion, this something is, from its most remarkable property, that of rendering a body combustible, properly enough denominated the food of fire, the *inflammable principle*, the *phlogiston*.

' From this analysis we may conclude, that the constituent parts

of *sulphur* are two—an *inflammable principle,* which is dispersed in the act of combustion, and an *acid.* . . .

' If you burn *charcoal* in the open air, and hold a glass over its flame, you will perceive that it burns without emitting either any watery vapour or sooty impurity, and nothing will remain, from a large portion of charcoal, but a small portion of white ashes, which are incapable of any further combustion; the principle effecting the combustion of the charcoal, and dispersed by the act of combustion, is the phlogiston.

' If you set *spirits of wine* on fire, they will, if pure, burn entirely away; they differ from charcoal in this, that they emit a vapour; but they leave no residuum. You may by proper vessels collect the vapour of burning spirits, and you will find it to be an insipid water, incapable of combustion. The principle effecting the combustion of the spirits of wine, and dispersed by the act of combustion, is the phlogiston.

' Some *metallic substances* burn, when sufficiently heated, with a flame more bright than that of spirits of wine, or charcoal: others burn or smother away like rotten wood, and most of them, when they have been kept in the open air in a proper degree of heat, lose their metallic appearance, and are converted into earth. Thus *red lead* is the earth procured from the burning of lead; and *putty* such as the polishers of glass and marble use, is the earth procured from tin; the principle effecting the combustion of metallic substances, and dispersed in the act of combustion, is the phlogiston.

' The *acid of the sulphur*; the *ashes of the charcoal*; the *water of the spirits of wine*; the *earths of metallic substances*, are utterly incapable of combustion; their respective differences from sulphur, charcoal, spirits of wine, and metallic substances, with respect, not only to inflammability, but to smell, colour, consistency, and other properties, are attributed to the phlogiston which is dispersed during the combustion of each of them.

' This inflammable principle, or phlogiston, is not one thing in animals, another in vegetables, another in minerals, it is absolutely the same in them all; just as water which enters into the composition of flesh, wood, coal, is still water, though its existence and homogeneity be rendered more doubtful in some substances than in others. This identity of phlogiston may be proved from a variety of decisive experiments; I will select a few, which may at the same time confirm what has been advanced concerning the constituent parts of sulphur.

' From the analysis or decomposition of sulphur effected by burning, we have concluded, that the constituent parts of sulphur are two—an *acid* which may be collected, and an *inflammable principle* which is dispersed; if the reader has yet acquired any

real taste for chemical truths, he will wish to see this analysis confirmed by synthesis; that is, in common language, he will wish to see sulphur actually made, by combining its acid with an inflammable principle.   It seldom happens that chemists can reproduce the original bodies, though they combine together all the principles into which they have analysed them; because not only the number and proportions of the principles, but the order also of their arrangement must be observed, before that can be effected; in the instance, however, before us, the reproduction of the origina' substance will be found complete.

' As the inflammable principle cannot be obtained in a palpabl< form separate from all other bodies, the only method by whicl we can attempt to unite it with the acid of sulphur, must be b\ presenting to that acid some substance in which it is contained Charcoal is such a substance, and by distilling powdered charcoa and the acid of sulphur together, we can procure a true yellov sulphur, in no wise to be distinguished from common sulphur This sulphur is formed from the union of the acid with the phlogistoı of the charcoal; and the charcoal may by this means be so entireh robbed of its phlogiston, that it will be reduced to ashes, as if i had been burned.   Animal substances reduced to the state of ɛ black coal, will, by being treated in the same way, yield sulphur. . .

' Lead, it has been observed, when melted in a strong fire, burn away like rotten wood; all its properties as a metal are destroyed and it is reduced to ashes.   If you expose the ashes of lead to ɛ strong fire, they will melt; but the melted substance will not be ɛ *metal*; it will be a yellow- or orange-coloured *glass*.   If you pounc this glass and mix it with charcoal dust, or if you mix the ashes o the lead with charcoal dust, and expose either mixture to a meltinȷ heat, you will obtain, not a *glass*, but a *metal*, in weight, colour consistency, and every other property the same as lead.   Thi operation, by which a metallic earth is restored to its metalli form, is called *Reduction*.   The ashes of lead melted *without* charcoa become *glass*; the ashes of lead melted *with* charcoal become ɛ *metal*; the charcoal, then, must have communicated something tҫ the ashes of lead, by which they are changed from a glass to a metal charcoal consists but of two things, of ashes, and of *phlogiston* the ashes of charcoal, though united with the ashes of lead, woulɩ only produce glass; it must therefore be the other constituent par of charcoal, or phlogiston, which is communicated to the ashes o lead, and by a union with which the ashes are restored to thei metallic form.   The ashes of lead can never be reduced to thei metallic form, without their being united with some matter con taining phlogiston, and they may be reduced to their metalliɩ form, by being united with *any* substance containing phlogiston iı

ı proper state, whether that substance be derived from the animal, vegetable, or mineral kingdom (for tallow, or iron-filings, may be substituted with success in the room of charcoal, in the experiment of reducing the ashes of lead), and thence we conclude, not only that phlogiston is a necessary part of a metal, but that phlogiston has an identity belonging to it, from whatever substance in nature it be extracted.'

It is clear from this extract that the phlogiston theory had no little success in explaining simple chemical phenomena. An unexpected relationship between superficially diverse facts was elegantly derived from a consideration of those facts in the light of the theory, and predictions made on a theoretical basis proved to be fulfilled when tested by experiment. The reactions of sulphur and sulphuric acid that WATSON describes can be so adequately explained in terms of phlogiston that we begin to understand the hold that the theory possessed over even the most brilliant chemists of the eighteenth century. It gained a further triumph by its explanation of the following phenomena. If zinc is dissolved in dilute sulphuric acid, a colourless inflammable gas is evolved and a solution of white vitriol remains. The inflammable gas was regarded as practically pure, though somewhat damp, phlogiston, and the reaction was explained by supposing that the acid split up the zinc into phlogiston (which was evolved) and zinc calx, the latter dissolving in the acid to form the white vitriol. A logical deduction from this hypothesis is that if zinc is first burned, so removing its phlogiston, the residual zinc calx should dissolve in dilute sulphuric acid, to yield a solution of white vitriol *without* evolution of the inflammable gas. Experiment shows, of course, that this deduction is correct, for the reaction takes place exactly as foretold.

Further, it follows from the phlogiston theory that if a metallic calx is heated in the above-mentioned inflammable gas, the metal ought to be regenerated—a deduction again in perfect agreement with experimentally established fact. Finally, the facts that a combustible substance will not burn in a vacuum, and that its flame is soon extinguished in a limited supply of air, were explained by assuming that a medium is necessary to absorb phlogiston, just as a sponge absorbs water.

As to the nature of phlogiston itself, since it proved impossible to isolate this 'inflammable principle' its properties had to be deduced from observation of the reactions in which it was supposed to take part—in exactly the same kind of way as the properties of fluorine were deduced long before the element itself was isolated. According to MACQUER, phlogiston is dry, volatile, very apt to assume an igneous movement, capable of combining with primitive principles such as earth and water—but in the latter case with much

more difficulty; it enters into the composition of an extremely large number of compounds, to which it gives the property of inflammability; it may pass from one compound to another; it is identical in whatever compound it may be found; and it is probably not ' elastic,' i.e. it does not behave as a gas.

Reflection on the phlogiston theory will show us that the real fault lay in the fact that chemists were still trying to explain the composition of material bodies in terms of *qualities*. Phlogiston was, in effect, the *quality* of inflammability rather than a material *principle* of inflammability; and though the importance of the theory can scarcely be overrated, in view of the large number of hitherto heterogeneous facts that it brought to a common denominator, it could never have attained its actual degree of success if BOYLE's destruction of the Aristotelian elements had been properly appreciated. As it was, the advantage that chemistry gained from phlogiston was considerable; but on looking back from our present standpoint we realize that even greater advantage would probably have accrued from its absence. This is the reason for the diametrically opposed views on phlogiston to be found in modern textbooks. Some writers plainly perceive that the phlogiston theory was undeniably a great triumph of theoretical chemistry; others maintain that it was a serious and unfortunate obstacle to chemical progress. Both views are justified: a brilliant success that prevents an even more brilliant is relatively a hindrance; and if it could be incontrovertibly proved that chemistry would have advanced more rapidly had phlogiston never appeared on the eighteenth-century scene, the universal opinion would of course be unfavourable to it.

The Chemistry of Gases.—We must now briefly consider some of the work on gases carried out by such men as BLACK (1728–99), SCHEELE (1742–86), CAVENDISH (1731–1810), and PRIESTLEY (1733–1804)—all of whom, it may be noted, were adherents of the phlogiston theory, though BLACK renounced it in 1791. A detailed account of the discoveries of these celebrated ' pneumatic chemists ' is here unnecessary, since, with the exception of BLACK, none of them made important contributions to chemical theory.

Until the eighteenth century was well advanced, the conception of gases as individual species of matter had gained little credence. The generally accepted belief was that any aëriform body differing from atmospheric air was air contaminated with various impurities. The old idea of qualities here crops up once more. Atmospheric air is the elastic fluid *par excellence*. If its usual qualities are removed or obscured, and new qualities are impressed upon it, the product is still ' air,' even though its properties are profoundly different. As late as the closing years of the century, such names

ıs ' fixed air ' ' mephitic air ' and ' inflammable aır ' were common ;urrency; and their disuse may be regarded as one of the turning-)oints of chemistry.

The word *gas* was invented by VAN HELMONT (p. 16), who was ;ufficiently in advance of his time to realize, if dimly, that atmo-;pheric air was only one example of a whole class of bodies. He ʻimself recognized two further examples, viz. *gas silvestre* and *gas* *bingue*. ' Gas silvestre ' was the name he applied to any gas e.g. CO_2) that would not support combustion, while ' gas pingue ' mplied any inflammable gas. This modest beginning had little ;equel until a century or so later, owing to the experimental lifficulties of manipulating gases. When, however, through the ʒfforts of a succession of workers, the pneumatic trough was finally ɔlaborated, progress became rapid; discovery after discovery came n quick succession, and the age of pneumatic chemistry had arrived.

BLACK'S classical research was upon carbon dioxide and its ʻeaction with quicklime and the caustic alkalis. His papers have ɔeen reprinted by the Alembic Club (A.C. Reprints, No. 1), and ;he student is strongly recommended to read them. The whole ınvestigation was a model of skilful experiment and brilliant logic, ıs may be realized by the fact that the results and explanations he ırrived at are those that we ourselves still accept. Summarily ʒxpressed, BLACK'S observations and deductions were as follows:

Observations:

    (i) When chalk is converted into quicklime a loss in weight occurs. [*Note the use of the balance: at that time quantitative work was rare.*]

   (ii) This loss in weight is due to evolution of a gas, *fixed air* [i.e. CO_2].

  (iii) Magnesia alba [a carbonate of magnesium] undergoes a similar loss in weight, and for a similar reason.

  (iv) Mild alkalis [Na_2CO_3 and K_2CO_3] suffer no such loss when heated, though, like chalk and limestone, they lose fixed air [CO_2] when treated with dilute acids.

Deductions :

    (i) Chalk, magnesia alba and the mild alkalis contain fixed air, which adheres to the last with very considerable force, but with less force to the other two.

   (ii) Chalk is a compound of limestone and fixed air, and magnesia alba a compound of magnesia [MgO] and fixed air.

Observations :

   (v) Quicklime absorbs water and dissolves to form lime-water.

  (vi) Lime-water turns milky on exposure to the air.

Deduction:

(iii) The air contains particles of fixed air that combine with the lime in the lime-water to form a precipitate of chalk.

Observations:

(vii) A certain weight of chalk yields a certain weight of lime when heated. If this lime is treated with a solution of mild alkali [K_2CO_3 or Na_2CO_3], it is reconverted into chalk, and the weight of chalk so obtained is equal to the original weight.

(viii) After filtering off the chalk, the solution left is a solution of *caustic* alkali [NaOH or KOH].

Deductions:

(iv) The lime took fixed air from the mild alkali.

(v) A mild alkali consists of caustic alkali and fixed air.

Confirmation of Deduction (v):

A solution of caustic alkali becomes converted into a solution of mild alkali when exposed to air, by absorption of particles of atmospheric fixed air.

BLACK's only other important chemical discovery was that of the bicarbonates, yet his work on carbon dioxide, quicklime, and alkalis was so great a masterpiece that he is justly regarded as one of the principal founders of chemistry. In particular, his recourse to the balance, as a servant and as an arbiter, at once raised his work to a much higher plane than that of most of his contemporaries, and set an example that never failed to produce fruitful results wherever it was followed.

SCHEELE, a German apothecary domiciled in Swedish Pomerania, was perhaps, of all in the annals of chemistry, the most versatile at discovery. Chlorine, oxygen, ammonia, hydrogen chloride, hydrogen fluoride, hydrogen sulphide, and arsenic trihydride (arsine) are among the gases that he was the first to isolate; while lactic, gallic, prussic, oxalic, citric, tartaric, malic, mucic and uric acids, pyrogallol, glycerol, and milk-sugar form a few of the organic compounds whose discovery or purification are due to him. Anticipating PRIESTLEY in the discovery of oxygen, he was deprived of priority in publication by the slowness of his publishers; but he went further than PRIESTLEY in showing that ordinary air consists of two kinds of gas. He noticed also that part of the air is lost in combustion, and observed that the residual air was relatively lighter than the original air. The part of the air which was lost during combustion he was unable to find again. He remarks that it might be suggested that ' the lost air still remains in the residual

air which can no more unite with phlogiston; for, since I have found that it is lighter than ordinary air, it might be believed that the phlogiston united with this air makes it lighter, as appears to be known already from other experiments. But since phlogiston is a substance, which always presupposes some weight, I much doubt whether such hypothesis has any foundation.' SCHEELE was closer than he realized to a supreme discovery, that was, in fact, made by the great Frenchman LAVOISIER in circumstances shortly to be described. In spite of occasional doubts and difficulties, SCHEELE never seriously suspected the phlogiston theory, even when LAVOISIER's historic experiments were creating a chemical revolution.

For our immediate purpose, the researches of CAVENDISH can be very briefly reviewed, though the reader will again be well advised to turn to the reprint of some of his chief papers (Alembic Club Reprints, No. 3) and study it carefully. One of CAVENDISH's principal discoveries was that of hydrogen (1766), which he called *inflammable air* and obtained by the action of dilute sulphuric acid or dilute hydrochloric acid upon zinc or iron. He proved further (1784) that water, instead of being an element, is a compound of inflammable air with dephlogisticated air (oxygen),. discovered a few years later than hydrogen by PRIESTLEY (p. 28). Finally he showed that nitric acid and nitre contain dephlogisticated air and phlogisticated air (nitrogen), and that atmospheric nitrogen contains traces of a constituent (argon) that will not combine with oxygen under the influence of the electric spark. Like SCHEELE, and like PRIESTLEY—to whom we must now turn—CAVENDISH was a disciple of phlogiston, and never retracted his allegiance, though this may have been because his mind had become absorbed in electrical problems by the time LAVOISIER's new theory of combustion was fully elaborated.

Dephlogisticated Air.—In August 1774 PRIESTLEY heated red calx of mercury (HgO) by means of a burning-glass. Much to his surprise, he obtained (*a*) mercury, and (*b*) a gas with the remarkable property of relighting glowing pieces of wood and of supporting combustion in general much better than ordinary air. If the reader has assimilated the main doctrines of phlogiston, he will be able to appreciate PRIESTLEY's amazement at such an entirely unexpected result. According to the phlogiston theory,

mercury calx=mercury—phlogiston.

Hence to convert mercury calx into mercury, the former must be supplied with phlogiston, and since PRIESTLEY had heated the calx entirely unmixed with any other substance, he was at a complete loss to account for the phenomenon. He was equally

unable to offer any suggestion as to the source of the gas that was evolved; but observing its striking power of supporting combustion he presumed it to be atmospheric air from which phlogiston normally present (as a result of the combustion of coal, wood, etc.) had been removed, and which had thus been conferred with the power of absorbing more phlogiston than it would ordinarily take up. In accordance with this view he named the gas *dephlogisticated air*. Not for a moment did he conceive the possibility that the facts might be explained upon some other theory than that of phlogiston. When the need for an explanation became urgent, he vacillated from one unsubstantial hypothesis to another, finally arriving at the following conclusion: In the formation of mercury calx from mercury, viz. by heating the metal in air for some considerable time to a temperature just below its boiling-point, the phlogiston of the metal unites with pure or dephlogisticated air from the atmosphere so as together to form a *fixed air* (which is not, in this case, carbon dioxide, as with BLACK). Hence the calx may be said to be mercury united with this fixed air. Then, in a greater degree of heat than that in which the union was formed, the fixed air is again decomposed; the phlogiston in it reviving the metal, while the pure or dephlogisticated air is set free. Consequently the mercury calx actually contains within itself all the phlogiston that is necessary to the revival of the mercury.

This involved suggestion is typical of the subsidiary hypotheses now becoming necessary to support the phlogiston theory in the light of intractable facts daily increasing in number and insistence. Some of these facts we may next consider.

Difficulties of Phlogiston.—In his *Cours de Chymie* (1675), LÉMERY mentions that ' in the calcination of lead and of several other substances there occurs an effect, which well deserves that some attention should be paid to it; it is that although by the action of the fire the sulphureous or volatile parts of the lead are dissipated, which should make it decrease in weight, nevertheless after a long calcination it is found that instead of weighing less than it did, it weighs more.' REY (1630) tells us that the same observation had been made by his friend BRUN; and indeed the fact had been known for centuries. BOYLE, in 1661, had put forward the suggestion that, in the process of calcination, ' multitudes of fiery corpuscles,' or particles of heat (then supposed to be a material substance), pass through the pores of the glass vessel in which the operation is carried out, and unite with metal undergoing calcination.

When the phenomenon was pressed upon the attention of phlogistian chemists, they countered the attack in three ways. In the first place, they replied that phlogiston had explained much, and

that therefore, though the increase in weight on calcination was at the moment inexplicable, the solution of the difficulty might safely be left to the future. There is nothing intrinsically reprehensible in the adoption of this attitude, which can usually be paralleled in the history of any theory and is, in fact, not dissimilar from the present position of the theory of the nature of electrons. At worst, it is merely a confession of weakness; at best, it represents that suspension of judgment which is a very desirable quality in a man of science faced with a conflict of evidence. It was certainly preferable to the second line of defence, which attempted to meet a prosaic fact by the adoption of a fantastic hypothesis, viz. that phlogiston had negative weight or 'levity.' 'Phlogiston,' said VENEL in his course of chemistry at the University of Montpellier, 'is not attracted towards the earth, but tends to rise; thence comes the increase in weight in the formation of metallic calces and the diminution in weight in their reduction.' The endowment of a supposititious entity with a uniquely improbable quality has little to recommend it as a method of advancing scientific knowledge; actually the suggestion received little support and the phlogistians themselves for the most part drew a decent veil over such a scientifically obscene episode.

A third explanation denied the reality of the supposed fact. According to the advocates of this view, the increase in weight was only apparent and was caused by the greater density of the calces than of the metals; on weighing in air, the smaller volume of air displaced by the calx made the apparent weight greater. It was conveniently forgotten that, in most cases, the calces have smaller densities than the metals from which they are formed.

In addition to those who advanced one or more of the above 'explanations,' there were many stalwarts who admitted the fact but resolutely declined to allow it any importance. Such a state of affairs may serve to remind us that the age of quantitative chemistry had not yet dawned, though the morning star of BLACK'S work heralded its near approach.

Reference has already been made to a further difficulty encountered by the phlogiston theory, viz. the necessity of air for combustion. BOYLE (1672) had shown that sulphur will not burn in a vacuum, and STAHL himself was fully aware that calcination of metals cannot be effected in vessels devoid of air. If combustion and calcination are essentially a mere disengagement of phlogiston, there would appear to be no reason why these processes should not take place equally well in a vacuum as in air, if not indeed better. The explanation advanced was, as we have seen, that air is necessary as an absorbent medium for the phlogiston; but this explanation failed to make clear the reason for the fact that, after combustion,

the residual air occupies a smaller volume than the original air. No satisfactory hypothesis to account for the last phenomenon was, in point of history, ever promulgated.

These and similar difficulties—such as the formation of water when a metallic calx is reduced in inflammable air, which was considered to be phlogiston united with a little heat—might have been expected to shake the faith of STAHL's disciples.   But, as PRIESTLEY himself remarked, ' we may take a maxim so strongly for granted that the plainest evidence of sense will not entirely change, and often hardly modify, our persuasions; and the more ingenious a man is, the more effectually he is entangled in his errors, his ingenuity only helping him to deceive himself by evading the force of truth.' Had PRIESTLEY applied this sententious aphorism to himself, WURTZ might have had no occasion to declaim, in later years, *La chimie est une science française: elle fut constituée par Lavoisier d'immortelle mémoire.*

The Overthrow of Phlogiston.—History affords us few examples of the complete reorientation of a science through the efforts of a single individual.   Such, however, was the feat triumphantly achieved by LAVOISIER (1743–94), who perished in the Revolution but surpassed it in significance.

The fortunate possessor of both a brilliant intelligence and ample wealth, LAVOISIER was ideally equipped for his task.   Early attracted to the study of problems of combustion, he soon confirmed and extended previous observations on the burning of substances in enclosed volumes of air.   Thus, on burning a piece of phosphorus under a bell-jar inverted in a trough of mercury, he made the following observations: (1) A limited volume of air will not burn an unlimited weight of phosphorus; (2) when an excess of phosphorus is used the flame is extinguished after a time, before the complete combustion of the phosphorus; (3) to relight the residual phosphorus, or to burn a fresh piece, the addition of more air is necessary; (4) a colourless solid, 'phosphoric acid,' is formed during the combustion; (5) after the completion of the reaction the residual air occupies about four-fifths of the original volume; (6) the weight of ' phosphoric acid ' produced is about two and a half times that of the phosphorus taken; and (7) the residual air is slightly lighter than ordinary air, and will no longer support combustion or life.

LAVOISIER followed up this line of experiment by further researches on the calcination of tin and lead.   It will be remembered that the increase in weight that occurs when tin and lead are burnt had already been observed many times, and was now common knowledge.   The only explanation that LAVOISIER regarded as at all satisfactory was that advanced by BOYLE, who

supposed that heat—which he considered a material substance—had passed through the vessel from the fire to the metal, thus causing the increase in weight. Reflection showed, however, that this hypothesis was easily susceptible of experimental proof or disproof, as LAVOISIER most lucidly explains:

'If,' he says, 'the increase in weight of metals calcined in closed vessels is due, as Boyle thought, to the addition of the matter of flame and fire which penetrates the pores of the glass and combines with the metal, it follows that if, after having introduced a known quantity of metal into a glass vessel, and having sealed it hermetically, one determines its weight exactly; and that if one then proceeds to the calcination in a charcoal fire, as Boyle did; and lastly that if one then reweighs the same vessel after the calcination, before opening it, its weight ought to be found to have increased by the whole of the quantity of the matter of fire which entered during the calcination.

'If, on the contrary . . . the increase in weight of the metallic calx is not due to the combination of the matter of fire nor to any exterior matter whatever, but to the fixation of a portion of the air contained in the space of the vessel, the vessel ought not to weigh more after the calcination than before, it ought merely to be found partly empty of air, and the increase in weight of the vessel should take place only at the moment when the missing portion of air is allowed to enter.'

LAVOISIER than proceeded to put his views to the test of experiment. He took a weighed glass flask, introduced a weighed quantity of tin, sealed the flask hermetically, and then heated it for an hour or two until no further calcination appeared to be taking place inside. He now allowed the flask to cool, after which he weighed it. There was no change in weight. Upon opening the flask, air was heard to rush in, and when the apparatus was weighed once more, an increase in weight was found. The actual figures obtained in the experiment are as follows:

	Onces	Gros	Grains
Weight of flask	12	6	51·75
Weight of flask *plus* tin	20	6	51·75
∴ Weight of tin	8	0	0·00

After calcination but before opening:

Weight of whole apparatus, unchanged.

After calcination and opening:

	Onces	Gros	Grains
Weight of whole apparatus	20	6	61·81
∴ Increase in weight on calcination . .	0	0	10·06

*B

LAVOISIER next removed the tin calx and residual tin from the flask and weighed them separately:

	Onces	Gros	Grains
Tin calx	2	7	2·75
Tin	5	I	7·25
Total weight after calcination . . .	8	0	10·00
But total weight before calcination . .	8	0	0·00
∴ Increase in weight on calcination . .	0	0	10·00

These results showed clearly that the increase in weight was due, not to the absorption of a hypothetical 'matter' of fire' as BOYLE had supposed, but to an absorption of air, the increase in weight of the metal being almost exactly equal to the weight of air which rushed in when the flask was opened.

Further experiments on the same lines led him to conclude:

' First, that one cannot calcine an unlimited quantity of tin in a given quantity of air.

' Second, that the quantity of metal calcined is greater in a large vessel than in a small one, although it cannot yet be affirmed that the quantity of metal calcined is exactly proportional to the capacity of the vessels.

' Third, that the hermetically sealed vessels, weighed before and after the calcination of the portion of tin they contain, show no difference in weight, which clearly proves that the increase in weight of the metal comes neither from the material of the fire nor from any matter exterior to the vessel.

' Fourth, that in every calcination of tin, the increase in weight of the metal is, fairly exactly, equal to the weight of the quantity of air absorbed, which proves that the portion of the air which combines with the metal during the calcination, has a specific gravity nearly equal to that of atmospheric air.

' I may add that, from certain considerations drawn from actual experiments made upon the calcination of metals in closed vessels, considerations which it would be difficult for me to explain to the reader without going into too great detail, I am led to believe that the portion of the air which combines with the metals is slightly heavier than atmospheric air, and that that which remains after the calcination is, on the contrary, rather lighter. Atmospheric air, on this assumption, would form, relatively to the specific gravity, a mean result between these two airs.'

His experimental figures enabled him to deduce that the air must consist of at least two gases, only one of which is concerned in calcination. By a measurement of the capacity of the flask, he was able to calculate the weight of air it originally contained.

This was considerably greater than the weight of air that entered when the flask was opened, the deduction therefore being that only a part of the air had been used. Now, since there was an excess of tin, the cessation of calcination before the whole of the air had been consumed could be explained only on the assumption that the air consists of a mixture of gases, of which one can effect calcination while the others cannot.

It was at this juncture that LAVOISIER met PRIESTLEY while the latter was on a visit to Paris (October 1774) and heard about the surprising experiment on red calx of mercury. How much information PRIESTLEY imparted to LAVOISIER is a matter of uncertainty, but it could not have been a great deal, for he had had but little time to investigate the properties of dephlogisticated air since discovering it in the previous August. However, a mere hint was sufficient for LAVOISIER, who, during the winter of 1774–5, repeated and extended PRIESTLEY's experiments. His first care was to confirm the generally accepted belief that red calx of mercury really is a calx, comparable in character to the calces of other metals. To do this, he heated an ounce of the substance with powdered charcoal in a small retort, and showed that mercury and fixed air (CO_2) were produced. Since this reaction—formation of metal and fixed air—is characteristic of calces when heated with charcoal, he felt justified in assuming that the red powder in question was definitely calx of mercury. He next heated some of the calx by itself, and observed that one ounce of it yielded seven gros and eighteen grains of liquid mercury and seventy-eight cubic inches of PRIESTLEY's dephlogisticated air. Investigation of the gas showed it to have the following properties:

   (i) It was insoluble in water, unlike fixed air.
   (ii) It would not turn lime-water milky, as fixed air does.
   (iii) It would not combine with alkalis, as fixed air does.
   (iv) It was able to bring about the calcination of metals.
   (v) It supported life and combustion very well.

These properties conclusively demonstrated that the gas was not fixed air, but that it was a gas 'purer' than atmospheric air. 'Hence it would appear to be proved,' he continues, 'that the principle which combines with metals during their calcination, and which increases their weight, is no other than the purest portion of the very air that surrounds us, that we breathe, and that passes during this operation [calcination] from the elastic state to the solid state. Hence the production of fixed air in all cases of metallic reductions with charcoal is due to the combination of the charcoal with the pure portion of the air; and it is very probable that all metallic calces would, like that of mercury, yield nothing but

" eminently respirable air " if one could reduce them all without addition [of any reducing agent], as one reduces red precipitate of mercury *per se* [HgO; calx of mercury]. . . .

' Since in the revivification of the mercury calx all the charcoal disappears and only mercury and fixed air are obtained, it is necessary to conclude that the principle hitherto called *fixed air* is the result of the combination of the eminently respirable portion of the air with the charcoal.'

Briefly expressed, LAVOISIER's conclusions from the experiments just mentioned were:

   (i) Mercury ' calx ' is a compound of mercury and ' eminently respirable air.'

   (ii) On heating, the calx decomposes into its constituents.

   (iii) Fixed air is a compound of carbon and ' eminently respirable air.'

   (iv) Mercury calx + carbon = mercury + fixed air.

These conclusions are, of course, those that we now accept; but LAVOISIER was not yet content. His main objective at the moment, to which the previous experiments were but a preliminary, was the composition of the atmosphere. It was in pursuit of this aim that he carried out the classical investigation described in his *Elementary Treatise on Chemistry*: an investigation of more consequence than any other single experiment in the history of chemistry. ' Lavoisier's Experiment,' to give it the name that marks it as his *chef d'œuvre*, was as follows—the words are those of LAVOISIER himself:
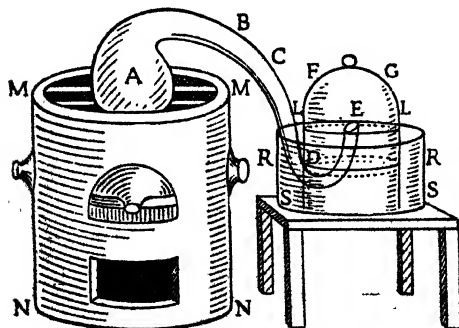
FIG. 1. LAVOISIER'S EXPERIMENT

' I took a matrass (A, Fig. 1) of about 36 cubical inches capacity, having a long neck BCDE, of six or seven lines internal diameter, and having bent the neck as in the figure, to allow of its being placed in the furnace MMNN, in such a manner that the extremity of its neck E might be inserted under a bell-glass FG, placed in a trough of quicksilver RRSS; I introduced four ounces of pure mercury into the matrass, and, by means of a syphon, exhausted the air in the receiver FG, so as to raise the quicksilver to LL, and I

carefully marked the height at which it stood, by pasting on a slip of paper. Having accurately noted the height of the thermometer and barometer, I lighted a fire in the furnace MMNN, which I kept up almost continually during twelve days, so as to keep the quicksilver always very near its boiling-point. Nothing remarkable took place during the first day: the mercury, though not boiling, was continually evaporating, and covered the interior surface of the vessel with small drops, at first very minute, which gradually augmenting to a sufficient size, fell back into the mass at the bottom of the vessel. On the second day, small red particles began to appear on the surface of the mercury; these, during the four or five following days, gradually increased in size and number, after which they ceased to increase in either respect. At the end of twelve days, seeing that the calcination of the mercury did not at all increase, I extinguished the fire, and allowed the vessels to cool. The bulk of air in the body and neck of the matrass, and in the bell-glass, reduced to a medium of 28 inches of the barometer and 54·5° of the thermometer, at the commencement of the experiment was about 50 cubical inches. At the end of the experiment the remaining air, reduced to the same medium pressure and temperature, was only between 42 and 43 cubical inches; consequently it had lost about one-sixth of its bulk. Afterwards, having collected all the red particles, formed during the experiment, from the running mercury in which they floated, I found these to amount to 45 grains.

' I was obliged to repeat this experiment several times, as it is difficult in one experiment both to preserve the whole air upon which we operate, and to collect the whole of the red particles, or calx of mercury, which is formed during the calcination. It will often happen in the sequel, that I shall, in this manner, give in one detail the results of two or three experiments of the same nature.

' The air which remained after the calcination of the mercury in this experiment, and which was reduced to five-sixths of its former bulk, was no longer fit either for respiration or for combustion; animals being introduced into it were suffocated in a few seconds, and when a taper was plunged into it, it was extinguished as if it had been immersed in water.

' In the next place I took 45 grains of red matter formed during this experiment, which I put into a small glass retort, having a proper apparatus for receiving such liquid, or gaseous product, as might be extracted. Having applied a fire to the retort in the furnace, I observed that, in proportion as the red matter became heated, the intensity of its colour augmented. When the retort was almost red-hot, the red matter began gradually to decrease in bulk, and in a few minutes after it disappeared altogether; at

the same time 41½ grains of running mercury were collected in the recipient, and 7 or 8 cubical inches of elastic fluid, greatly more capable of supporting both respiration and combustion than atmospherical air, were collected in the bell-glass.

' A part of this air being put into a glass tube of about an inch diameter, showed the following properties: A taper burned in it with a dazzling splendour, and charcoal, instead of consuming quietly as it does in common air, burnt with a flame, attended with a decrepitating noise, like phosphorus, and threw out such a brilliant light that the eyes could hardly endure it. This species of air was discovered almost at the same time by Dr. Priestley, Mr. Scheele, and myself. Dr. Priestley gave it the name of *dephlogisticated air*, Mr. Scheele called it *empyreal air*; at first I named it *highly respirable air*, to which has since been substituted the term of *vital air*. We shall presently see what we ought to think of these denominations.

' In reflecting upon the circumstances of this experiment, we readily perceive, that the mercury, during its calcination, absorbs the salubrious and respirable part of the air, or, to speak more strictly, the base of this respirable part; that the remaining air is a species of mephitis, incapable of supporting combustion or respiration; and consequently that atmospheric air is composed of two elastic fluids of different and opposite qualities. As a proof of this important truth, if we recombine these two elastic fluids, which we have separately obtained in the above experiment, viz. the 42 cubical inches of mephitis, with the 8 cubical inches of respirable air, we reproduce an air precisely similar to that of the atmosphere, and possessing nearly the same power of supporting combustion and respiration, and of contributing to the calcination of metals.'

LAVOISIER was fully alive to the revolutionary character of the conclusions at which he had arrived. Writing in 1778, he prefaces a first cautious attack on phlogiston by some unexceptionable remarks on the nature of scientific hypotheses and theories in general. Theoretical systems in physical science, he urged, are nothing more than instruments with which to succour the weakness of our senses; properly speaking, they are methods of approximation that put us on the road to the solution of the problem. They are hypotheses that, if successively modified, corrected and changed in accordance with the demands of experimental fact, will unfailingly lead us to a knowledge of the true laws of nature.

After this (unsuccessful) attempt to disarm opposition, he sets out his new theory of combustion, according to which:

(i) The active agent in combustion is PRIESTLEY's dephlogisticated air.

(ii) This ' air,' better named ' eminently respirable air,' is con-
tained in the atmosphere to the extent of approximately
one-sixth part by volume, and is the only part of the
atmosphere capable of supporting combustion.

(iii) When a substance burns, it absorbs eminently respirable
air, and the increase in weight is exactly equal to the weight
of this air taken up.

(iv) On calcination,

metal+eminently respirable air=metallic calx,
(element)   (compound)

not, as the phlogiston theory has it,

metal—phlogiston   =metallic calx.
(compound)   (element)

LAVOISIER's theory at first gained little headway, but in 1783
he made a second onslaught in his *Reflections on Phlogiston.* In
the meantime he had shown that the combination of moist eminently
respirable air with sulphur yielded sulphuric acid, with phosphorus
phosphoric acid, and with carbon carbonic acid. Regarding the
gas as the essential principle of acids, he accordingly changed its
name to *oxygen.*

In the celebrated *Reflections* he threw caution to the winds,
maintaining that his *principe oxygène* explained ' the chief diffi-
culties of chemistry ' with an astonishing simplicity—a claim that
we must admit to have been perfectly true. ' But if in chemistry
everything can be satisfactorily explained without the help of
phlogiston, by that fact alone it is exceedingly probable that such
a principle does not exist, that it is a hypothetical entity, a
gratuitous supposition; now, one of the principles of sound logic
is not to multiply entities unnecessarily. Perhaps I might have
confined myself to these negative proofs, and stayed content with
having proved that the phenomena can be better explained without
phlogiston than with it; but it is time for me to express myself in
a more precise and formal manner concerning an opinion that I
regard as an error fatal to chemistry, an error that seems to me
to have considerably retarded progress by the unsound method
of reasoning it has introduced. . . . It is time to recall chemistry
to a more rigorous method of reasoning; to strip the facts with which
this science is enriched every day from that which reasoning and
prejudices add thereto; to distinguish fact and observation from
that which is systematic and hypothetical; finally, to mark the
limit, so to speak, to which chemical knowledge has arrived, in
order that those who follow us may set out with confidence from
this point to advance the science. . . . Chemists have made of

phlogiston a vague principle which is not rigorously defined, and which consequently adapts itself to all explanations into which it may be brought. Sometimes this principle is heavy, and sometimes it is not; sometimes it is free fire, sometimes it is fire combined with the earthy element; sometimes it passes through the pores of vessels, and sometimes they are impenetrable for it. It explains at once causticity and non-causticity, transparency and opacity, colours and the absence of colours. It is a veritable Proteus which changes its form at every instant.'

After the publication of this article, LAVOISIER rapidly won over to his side the majority of his fellow-chemists, though he suffered much opposition from PRIESTLEY and certain others among the older men. His victory was hard-won, and the reader should not imagine that there was anything in the nature of enthusiasm to abandon phlogiston for oxygen. Indeed, if space allowed, we should find it extremely instructive to follow the fortunes of the battle from stage to stage; but since this is not possible, we must content ourselves by pointing out that, though the phlogiston theory was overthrown, the *facts* that the phlogistian chemists, had ascertained and systematized remained a permanent acquisition to the stock of human knowledge. It is sometimes argued, even by cultured minds, that no reliance is to be placed upon the voice of science, since her theories are continually changing. Such an attitude is entirely unjustifiable, (*a*) since the accumulation of experimentally confirmed facts progresses steadily in spite of the fate of theories; (*b*) since whenever a new theory replaces an old one, a wider sweep of facts is brought into the region of ordered arrangement; and (*c*) since the fate of the old theory is more often than not merely an absorption into the more comprehensive system that succeeds it, as a rough approximation is implicit in a closer one.

With the establishment of the oxygen theory of combustion, chemistry was already beginning to present a more familiar aspect, and we may therefore now proceed to discuss the second great pillar of the nineteenth-century form of the science, viz. the atomic theory of DALTON. Those who wish to follow the important work that was carried out, in the closing years of the eighteenth century and the opening years of the nineteenth, upon qualitative and quantitative analysis, and upon descriptive inorganic chemistry in general, are referred to the standard histories of chemistry mentioned at the end of this Historical Introduction.

The Atomic Theory.—The development of the atomic theory, like that of the phlogiston theory, should be closely followed by the student of chemistry, since it clearly demonstrates the temporary and provisional character of scientific theories and hypotheses and makes the pragmatic nature of scientific truth sufficiently plain

even to those innocent of formal philosophy. Much has been written on the method of science that has no particular value for scientists themselves; what it *is* essential for scientists to realize is that no theory is sacrosanct and no authority infallible. Though deduction from facts to a law, followed by induction from the law to further facts previously undiscovered, is the common course of scientific progress, such a method is not confined to science, and when scientists follow it they frequently do so unconsciously. The condition of scientific advance is not adherence to formal philosophic method but the spirit of free inquiry supported by experimental confirmation. Atoms, ions, and electrons are but scientific fictions—convenient names for packets of associated phenomena—and the more quickly the young chemist learns to respect them as tools, not to worship them as eternal verities, the more quickly will he fit himself for productive original investigation.

It is obvious that, if matter is not continuous, it must be discrete. Yet in classical Greece, where the Western form of the atomic theory originated, the problem did not present itself as quite such a simple choice between opposites. There were felt to be serious objections to the hypothesis of the unbroken continuity of matter, but the human mind had not yet accustomed itself to the notion of a void, a completely empty space. Consequently, when the theory arose that matter is composed of discrete atoms, that it has in fact a ' grained ' structure, the conception was so foreign that at first it won little acceptance. Atoms were conceivable, but what was between them? To reply ' Empty space ' appeared suspiciously like shirking the issue. However, the labours of LEUCIPPUS and DEMOCRITUS (fifth century B.C.) and EPICURUS (about 300 B.C.) at length succeeded in making the idea of a void familiar, and the atomic theory that they developed then received respectful attention. Our knowledge of the theory is derived mainly from the poem of LUCRETIUS (first century B.C.), in which the earlier views are logically marshalled and brilliantly expounded. The chief points of permanent value, in the light of subsequent developments, are as follows:

(i) There is only one ultimate species of matter.

(ii) Matter is indestructible and cannot be created.

(iii) Matter is not continuous, but discrete, i.e. it has a ' grained ' structure.

(iv) Matter is composed of ' atoms ' which are invisible, physically indivisible, indestructible, eternal and impenetrable.

(v) Between atoms there is simply a void—empty space.

(vi) The atoms of different substances are different in shape, size and weight.

(vii) Atoms are in constant motion—rectilinear according to DEMOCRITUS—colliding with, and rebounding from, one another ' like motes in a sunbeam.'

(viii) Substances differ in properties according to the nature, number and arrangement of the atoms of which they are composed.

When it is put thus baldly, we may be tempted to read into the classical theory a good deal that it does not actually contain. Yet this temptation must be resisted. ' It must always be remembered that ancient speculation is a very different matter from modern research: at its best it rested in the main upon *a priori* reasoning, and though observation and even experiment may have given some knowledge of detail, they had little place in the development of the larger fundamental theories. And not only do methods differ, but the fundamental conceptions of the atom in the ancient theory and modern chemistry are widely divergent. The Greeks conceived a perfectly hard unalterable body, incapable of entering into any combination except by juxtaposition or at most entanglement: modern chemistry conceives an elastic changeable body, which in the fusion of chemical combination merges its material identity in a new substance.' [1] In spite of this radical difference between the ancient and the modern forms of the atomic theory, the Greeks must nevertheless be given the credit for having familiarized men with the abstruse conceptions of atoms that had parts and were yet indivisible and of a void that was literally void. How strange these conceptions appeared to be when first suggested we may perhaps appreciate by the fact that ARISTOTLE (384–322 B.C.) —the greatest scientific mind of antiquity—himself regarded the first as anomalous and the second as incredible. All the weight of his authority was consequently thrown against the atomic theory, and when GALEN, the celebrated physician of the second century A.D., added his veto to that of ARISTOTLE, atoms suffered an eclipse that was to last for some fourteen hundred years. The eclipse was, however, not absolutely total. Sporadically, among the Moslem scientists and among the scholars of medieval Christendom, the atomic conception of matter received momentary attention; and though the idea was resuscitated only to be immediately disavowed, the continuity of its existence remained unbroken until the revival of atomism in the seventeenth century.

One of the principal protagonists of atoms at this period was GASSENDI (1592–1655), who combined a violent antipathy to ARISTOTLE with a warm admiration for EPICURUS. He urged the atomic theory of the latter with considerable persuasive skill, and

[1] C. Bailey, *The Greek Atomists and Epicurus* (1928), pp. 4-5.

as he was fortunate enough to find a foeman worthy of his steel in
DESCARTES (1596–1650), the passages-at-arms between them brought
atoms once more into the forefront of the public gaze.   DESCARTES
was not an anti-atomist, but, like ARISTOTLE, he could not admit
the possibility of truly vacuous space.   Neither would he allow
that atoms were indivisible, regarding them rather as liable to be
worn away into a still more tenuous matter by mutual friction.
' If we assume,' he says, ' that all the matter of which the world
is made up, had at the beginning been divided into many equal
parts, then these could not at first have been all round, because
spheres joined cannot constitute an entirely solid and continuous
body such as this universe, in which . . . void cannot exist.   But
whatever the original shape of these parts may have been, they
must in time have become round because they are endowed with
rotatory motions of different kinds, and so by and by as they col-
lided their corners were ground away.'   But inasmuch as empty
space can exist nowhere in the universe, it follows that the spaces
between the particles must be filled with a subtle, extremely finely
divided matter, derived from the particles themselves by friction.
Finally, DESCARTES postulated a third sort of matter, consisting
of parts more coarse than either the interstitial matter or the
spherical particles.

In the Cartesian interstitial matter or *materia coelestis* we may
see a forerunner of the ' ether '—that ' subject of the verb *to
undulate*' with which nineteenth-century science, unable like
ARISTOTLE to conceive of an absolute void, filled the whole of
space.   In its main structure, however, the system of DESCARTES
was of no immediate scientific value: it is, as usual, to the men of
science that we must have recourse for theories that lead to definite
results.   The immediate service that DESCARTES and GASSENDI
rendered to science was that they brought the atomic hypothesis
of the structure of matter into such prominence that no chemist
could remain in ignorance of it.   We find evidence of this fact in
the writings of BOYLE, who refers to the hypothesis that ' the
World is made up of an innumerable multitude of singly insensible
Corpuscles, endow'd with their own Sizes, Shapes, and Motions,'
in terms which imply that it was perfectly familiar to his con-
temporaries.   It gained further consideration from men of science
when NEWTON (1642–1727) declared his allegiance.

In his *Opticks*, NEWTON says: ' It seems probable to me that
God in the beginning formed matter in solid, massy, hard, im-
penetrable, moveable particles, of such sizes and figures, as most
conduced to the end for which He formed them; and that these
primitive particles, being solids, are incomparably harder than any
porous bodies compounded of them; even so very hard as never

to wear or break in pieces, no ordinary power being able to divide what God Himself made one in the first creation. . . . God is able to create particles of matter of several sizes and figures, and in several proportions to the space they occupy, and perhaps of different densities and forces. . . . Now, by the help of these principles, all material things seem to have been composed of the hard and solid particles above mentioned—variously associated in the first creation, by the counsel of an intelligent agent.'

This passage is very reminiscent of LUCRETIUS, but NEWTON was a scientist and applied his hypothesis to experimental fact. BOYLE had recently discovered his 'Law,' and NEWTON offered a theoretical explanation of the phenomenon in ' the first quantitative conclusion ever formed about atoms.' He proved in the *Principia* that ' if the density of a fluid gas which is made up of mutually repulsive particles is proportional to the pressure, the forces between the particles are reciprocally proportional to the distances between their centres. And vice versa, mutually repulsive particles, the forces between which are reciprocally proportional to the distances between their centres, will make up an elastic fluid, the density of which is proportional to the pressure.' NEWTON goes on: ' Whether elastic fluids do really consist of particles so repelling one another, is a physical question. We have here demonstrated mathematically the properties of fluids consisting of this kind, that hence philosophers may take occasion to discuss that question.'

What strikes us immediately is the great difference in attitude towards the atomic theory, between the scientists as exemplified by NEWTON and the general body of atomic philosophers. It is perfectly true to say that the atomic theory can be traced, in unbroken historical continuity, from LEUCIPPUS to NEWTON, but NEWTON's position is this: ' Let us *suppose* that there are atoms and see what may be deduced therefrom in accordance with experimental fact,' and therein lies the vital difference between a scientific theory and a philosophic speculation.

Newton's suggestion that a gas may be composed of particles which repel one another in a perfectly definite way was the immediate cause of the formulation of the chemical atomic theory a century later.

The Atomic Theory of Dalton.—Though the atomic theory, in its philosophical form, had been in existence for over two thousand years before the birth of JOHN DALTON (1766–1844), he it was who first moulded it into such a form that it became susceptible of experimental verification. For this reason DALTON is rightly regarded as the founder of the modern atomic theory. It is true that WILLIAM HIGGINS (d. 1825) published ideas of a somewhat

similar nature to those of DALTON about fourteen years earlier than the latter, but their importance was not realized at the time (1789)—owing to the controversy over phlogiston—and the lack of interest shown in his work discouraged HIGGINS from continuing it. The same fate, it will be remembered, befell NEWLANDS in connection with his *Law of Octaves*; yet though HIGGINS must be credited with priority over DALTON in certain essential points, there is no doubt that DALTON elaborated his theory quite independently. As to the subsequent developments, which formed the greater part of DALTON's theory, there is no reason to suppose that HIGGINS foresaw them or that he would have had the genius to carry them to the fulfilment they reached at the hands of DALTON.

The sequence of events that led DALTON to the formulation of his theory is not quite clear, and since he himself gave contradictory accounts on different occasions it is very unlikely that the truth of the matter will ever be known. The reader who is interested in the subject is referred to the histories of chemistry; from the present point of view the actual sequence is of little importance in comparison with the main features of the theory in its final form. Through a fondness for meteorology, DALTON was led to a study of the properties and composition of the atmosphere, and thence to an investigation of ' elastic fluids ' or gases in general. Steeped in the works of NEWTON, he habitually thought in terms of atoms, and the atomic theory seems to have first taken shape in his mind as a physical theory to explain the properties of gases. ' Having long been accustomed to make meteorological observations,' he said, ' and to speculate upon the nature and constitution of the atmosphere, it often struck me how a *compound* atmosphere, or a mixture of two or more elastic fluids, should constitute apparently a homogeneous mass, or one in all mechanical relations agreeing with a simple atmosphere. Newton has demonstrated clearly in the 23rd Prop. of Book II of the *Principia* that an elastic fluid is constituted of small particles or atoms of matter which repel each other by a force increasing in proportion as their distance diminishes.'

Applying Newtonian principles to the problem of mixed gases, he was able to account for a phenomenon he had observed in 1801, viz. that the pressure in a mixture of gases is the sum of the partial pressures, or that in such a mixture each gas exerts the same pressure as it would if it were separately enclosed in the volume occupied by the whole mixture. This he explained by assuming that when two gases, ' denoted by A and B, are mixed together, there is no mutual repulsion amongst their particles, that is, the particles of A do not repel those of B, as they do one another.' Although this explanation is no longer held, it shows

that DALTON was already employing an atomic hypothesis, and that he was profoundly influenced by the ideas of NEWTON. Two years later, DALTON was able to publish a further generalization, which stated that if a mixture of gases is exposed to a liquid, each gas dissolves in the liquid according to its partial pressure.

From the mental picture he had formed of the atomic constitution of gases, DALTON was led to ponder the possibility of an experimental determination of the relative weights of atoms of different kinds. It was here that his genius at once made itself apparent. Having discovered that carbon dioxide contained twice as much oxygen, for a given quantity of carbon, as carbonic oxide [carbon monoxide], he made the bold assumption that the ' compound atom ' of carbonic oxide consisted of one atom of carbon and one of oxygen, and that the ' compound atom ' of carbon dioxide consisted of one atom of carbon and two of oxygen. If this assumption were correct, then the ratio by weight of oxygen to carbon in carbonic oxide must be the same as the relative weights of the atoms of these two elements. Similar groups of compounds for which DALTON obtained analytical data were olefiant gas [C_2H_4] and methane [CH_4]; and nitrous gas [NO], nitrous oxide [N_2O], and ' nitric acid ' [NO_2]. He found that the same kind of relation held, viz. that when two or more elements combine to form more than one compound, then the different weights of one element that combine with a fixed weight of the other are in a simple ratio to one another; he had, in fact, discovered the *Law of Multiple Proportions*, though he never gave the law formal expression. In the light of this important result, he was able to make conjectures as to the structures of the ' compound atoms ' of the substances in question, and thus to arrive at provisional atomic weights for the elements contained in them. His note-book contains the following list, under the date 6th September, 1803:

Hydrogen	.	1
Oxygen .	.	5·66
Azote (nitrogen)	4
Carbon .	.	4·5
Sulphur .	.	17

together with the weights of certain ' compound atoms ':

Water	6·66	' Nitric acid ' [NO_2]	15·32
Ammonia .	5	Sulphurous acid [SO_2]	22·66
Nitrous gas [NO]	9·66	Sulphuric acid [SO_3]	28·32
Nitrous oxide	13·66	Carbonic acid [CO_2]	15·8
		Oxide of carbon [CO]	10·2

DALTON gave a further exposition of his theory in Chapter III, ' On Chemical Synthesis,' of Part I of his epoch-making work, *A New*

System of Chemical Philosophy (1808). The chief points are as follows:

1. All matter is composed of a great number of extremely small particles or *atoms*. To attempt to conceive the number of particles is like attempting to conceive the number of stars in the universe; we are confounded by the thought. But if we limit the subject, by taking a given volume of a gas, we seem persuaded that, let the divisions be ever so minute, the number of particles must be finite; just as in a given space of the universe, the number of stars and planets cannot be infinite.

2. Chemical analysis and synthesis go no farther than to the separation of particles one from another, and to their reunion. In other words, atoms are indestructible and cannot be created, whence may be deduced the *Law of the Conservation of Matter*, viz. matter can neither be created nor destroyed. ' No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen. All the changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance.'

3. Each element has its own distinctive kind of atom, and similarly each compound has its own distinctive kind of ' compound atom ' or ultimate mechanical particle. Thus, any one atom of iron exactly resembles any other atom of iron, but is different from the atoms of all other elements; and all ' compound atoms ' of water exactly resemble one another but differ from the ' compound atoms ' of all other compounds.

4. It is important, and possible, to ascertain the relative weights of different atoms. ' In all chemical investigations, it has justly been considered an important object to ascertain the relative weights of the simples [elements] which constitute a compound. But unfortunately the inquiry has terminated here; whereas, from the relative weights, the relative weights of the ultimate particles or atoms of the bodies might have been inferred, from which their number and weight in various other compounds would appear, in order to assist and to guide future investigations, and to correct their results. Now it is one great object of this work, to show the importance and advantage of ascertaining the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle.'

5. When elements combine to form compounds, the ultimate particles of the compounds consist of *small* whole numbers of the

atoms of the elements concerned.   Thus if there are two elements, *A* and *B*, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple:

  1 atom of A+1 atom of B=1 ultimate particle of C, a binary
    compound.
  1 atom of A+2 atoms of B=1 ultimate particle of D, a ternary
    compound.
  2 atoms of A+1 atom of B=1 ultimate particle of E, a ternary
    compound.
  1 atom of A+3 atoms of B=1 ultimate particle of F, a quater-
    nary compound.
  3 atoms of A+1 atom of B=1 ultimate particle of G, a quater-
    nary compound.

At this stage DALTON had no means of determining the actual numbers of atoms in the ultimate particles of compounds, so that he had to fall back on assumptions.   The main assumptions that he made were these:

  ' 1st. When only one combination [compound] of two elementary bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary.

  ' 2nd. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.

  ' 3rd. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*.

  ' 4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, etc.

  .   .   .   .

  ' 7th. The above rules and observations apply, when two compound bodies, such as C and D, D and E, etc., are combined.'

These assumptions were clearly justifiable, since they led to deductions that could easily be tested by direct experiment.   Should the experimental results have been unfavourable, it would of course have been necessary to modify the assumptions made.

DALTON's method of applying his principles may best be understood by a consideration of some typical examples:

  Water.—At that time water was the only compound of hydrogen and oxygen known.   Hence, he says, we conclude ' that water is a binary compound of hydrogen and oxygen [i.e. the ultimate particle of water is composed of one atom of hydrogen and one of oxygen], and the relative weights of the two elementary atoms are as 1 : 7, nearly ' [1 : 7 since his analytical data gave this ratio as the ratio by weight of hydrogen to oxygen in water].

Ammonia.—Ammonia was the sole compound of hydrogen and nitrogen known to DALTON, who thus regarded it, on his system, as a binary compound of the two elements; and since his analysis of the gas gave the ratio by weight of 1 hydrogen to approximately 5 nitrogen, he concluded that the atomic weight of nitrogen was 5.

Oxides of Nitrogen.—According to DALTON, the composition of the ultimate particles of the oxides of nitrogen was:

Nitrous gas [NO].	Binary. One atom of nitrogen and one atom of oxygen.
' Nitric acid ' [NO$_2$].	Ternary. One atom of nitrogen and two atoms of oxygen.
Nitrous oxide [N$_2$O].	Ternary. Two atoms of nitrogen and one atom of oxygen.
' Nitrous acid ' [N$_2$O$_3$].	A compound of ' nitric acid ' and nitrous gas.
' Oxynitric acid ' [N$_2$O$_5$].	A compound of ' nitric acid ' and oxygen.

Oxides of Carbon.—These have already been mentioned (p. 44). DALTON considered carbonic oxide [CO] to be binary and carbonic acid [CO$_2$] ternary. By quantitative analysis it was thus easy to arrive at the relative weights of the oxygen and carbon atoms.

Working in this way, DALTON was able to extend his list of relative weights of the ultimate particles of elements; and it is important to note that he made what was then the by no means self-evident assumption that the weight of a ' compound atom ' is equal to the sum of the weights of the elementary atoms composing it. The idea that heat was a material substance (' caloric ') was still held, and DALTON's tacit neglect of the heat evolved or absorbed in chemical reactions, as far as any possible change in weight was concerned, is a noteworthy feature of his method.

DALTON's improved and lengthened list of the relative weights of ultimate particles, as given at the end of the *New System*, Part I (2nd edition, 1842), is as follows:

Hydrogen	. .	1	Strontites [SnCO$_3$].		46
Azote .	. .	5	Barytes [BaSO$_4$]	.	68
Carbone	. .	5	Iron .	. .	38
Oxygen	. .	7	Zinc .	. .	56
Phosphorus	. .	9	Copper	. .	56
Sulphur	. .	13	Lead .	. .	95
Magnesia	. .	20	Silver .	. .	100
Lime .	. .	23	Platina	. .	100
Soda .	. .	28	Gold .	. .	140
Potash	. .	42	Mercury	. .	167

A glance at the table on p. 47 will show that DALTON's values are in many cases very different from those accepted at the present day. This is partly due to inaccurate analysis, but a little consideration will make it apparent that the real difficulty lay in the fact that DALTON had *no conclusive means of arriving at the number of atoms in the ultimate particle of any compound*. Thus he assumed, in the absence of evidence to the contrary, that the ultimate particle of water contains only 1 atom of hydrogen and 1 of oxygen, and hence obtained, by deduction from the data supplied by quantitative analysis, the number 7 [accurate value, of course, 8] for the atomic weight of oxygen. It is, however, obvious that if the ultimate particle of water consists of 2 atoms of hydrogen and 1 of oxygen, then the atomic weight of the latter will be 14, while if it consists of 3, 4, 5, etc., atoms of hydrogen and 1 of oxygen, the atomic weight of oxygen must be 21, 28, 35, etc. In the same way, by regarding the ultimate particle of ammonia to consist of 1 atom of hydrogen and 1 of nitrogen, DALTON obtained ' about 5 ' for the atomic weight of nitrogen, instead of the modern value 14—which is based upon the fact that 1 molecule or ultimate particle of ammonia consists of 1 atom of nitrogen combined with not 1 but 3 atoms of hydrogen.

This lack of knowledge of the number of atoms in the ultimate particle of a compound was a serious hindrance to the development of the theory. DALTON himself was fully alive to the difficulty, and even as late as 1827 expresses himself as quite frankly dissatisfied with the position. ' The second object of the atomic theory,' he writes, ' namely, that of investigating the *number* of atoms in the respective compounds, appears to me to have been little understood, even by some who have undertaken to expound the principles of the theory.

' When two bodies, A and B, combine in multiple proportions; for instance, 10 parts of A combined with 7 of B to form one compound, and with 14 to form another, we are directed by some authors to take the smallest combining proportion of one body as representative of the elementary particle or atom of that body. Now it must be obvious to any one of common reflection, that such a rule will be more frequently wrong than right. For, by the above rule, we must consider the first of the combinations as containing 1 atom of B and the second as containing 2 atoms of B, with 1 atom or more of A; whereas it is equally probable by the same rule that the compounds may be 2 atoms of A to 1 of B, and 1 atom of A to 1 of B respectively; for, the proportions being 10 A to 7 B (or, which is the same ratio, 20 A to 14 B) and 10 A to 14 B, it is clear by the rule, that when the numbers are thus stated, we must consider the former combination as composed of 2 atoms of

A, and the latter of 1 atom of A, united to 1 or more of B. Thus there would be an *equal* chance for right or wrong. But it is possible that 10 of A, and 7 of B, may correspond to 1 atom A, and 2 atoms B; and then 10 of A, and 14 of B, must represent 1 atom A, and 4 atoms B. Thus it appears the rule will be more frequently wrong than right. It is necessary not only to consider the combination of A with B, but also those of A with C, D, E, . . . before we can have good reason to be satisfied with our determinations as to the *number* of atoms which enter into the various compounds. Elements [compounds] formed of azote [nitrogen] and oxygen appear to contain portions of oxygen, as the numbers 1, 2, 3, 4, 5 successively, so as to make it highly improbable that the combinations can be effected in any other than one of two ways. But in deciding which of those two we ought to adopt, we have to examine not only the compositions and decompositions of the several compounds of these two elements, but also compounds which each of them forms with other bodies. I have spent much time and labour upon these compounds, and upon others of the primary elements, carbon, hydrogen, oxygen, and azote, which appear to me to be of the greatest importance in the atomic system; but it will be seen that I am not satisfied on this head, either by my own labour or that of others, chiefly through want of an accurate knowledge of combining proportions.'

How this difficulty was at length overcome we shall learn in a moment. We may, however, first turn aside to see that the simple laws of chemical combination are all to be deduced from the atomic theory. In point of fact, they were discovered independently of it, and the fact that they were experimentally established afforded strong presumptive evidence in its favour.

1. *The Law of the Conservation of Matter.*—This follows from the postulates that matter is composed of atoms and that atoms are indestructible and uncreatable.

2. *The Law of Constant Composition.*—If all the ultimate particles of a given compound are identical, the compound must have an invariable composition.

3. *The Law of Multiple Proportions.*—This follows from DALTON'S assumption that when atoms of elements combine to form the ultimate particles of compounds, they do so in *small* whole numbers.

Suppose, for example, that the elements A and B unite together to form two different compounds. The simplest imaginable case will be when in one of the compounds the ultimate particle consists of one atom of A and one of B, and in the other compound the ultimate particle consists of one atom of A and two of B. Since, in one ultimate particle of each of these two compounds there is

one atom of A, it follows that the weight of A is constant in the two particles. The weights of B, on the other hand, will be in the ratio of the numbers of atoms of B respectively present in the particles; in this instance, 1 & 2. This is a simple ratio, and if compounds are always composed of *small* numbers of atoms, the ratio will always be a ratio of small numbers and therefore a simple one.

Although DALTON never gave this law formal   ression, there is no doubt whatever that he thoroughly underst   it, and that it was, indeed, an important factor in the develop   t of the atomic theory (*see* p. 44). The law was completely estab   ed, for large numbers of compounds, by BERZELIUS (1779–1848).

4. *The Law of Reciprocal Proportions*, also a logical deduction from the theory, states that if an element A combines with an element B and also, separately, with an element C, then if B and C also combine together, the proportion by weight in which they do so will be simply related to the ratio of the weights of B and C which combine, separately of course, with a constant weight of A. The necessity of this relation will be obvious when it is remembered that DALTON postulated (*a*) that combination takes place between small numbers of atoms, to form the ultimate particles of compounds, and (*b*) that all the atoms of the same element are of exactly the same weight. Particular instances of the law were observed by RICHTER (1762–1807), but it was again BERZELIUS who thoroughly established it.

A further debt that chemists owe to BERZELIUS is the introduction of the modern system of symbols, formulae and equations. DALTON's notation, consisting of circles with various kinds of shading, etc., was clumsy, forbidding, and extremely liable to error; and its replacement by the simple scheme of BERZELIUS must be regarded as an important factor in the success of the atomic theory.

Gay-Lussac's Law.—The first step towards the solution of DALTON's difficulty in arriving at the number of atoms in the ultimate particle of a compound was taken by GAY-LUSSAC (1778–1850), who in 1808 enunciated his well-known law of the combination of gases by volume, viz. that when gases react they do so in volumes that bear a simple ratio to one another and to the volume of the product if that is gaseous.

This simple relation between the volumes of reacting gases appeared to have some underlying significance, and BERZELIUS tentatively advanced the hypothesis that equal volumes of gases contain equal numbers of atoms. As a matter of fact, DALTON, in the course of his reflections upon atoms, had already taken this idea into consideration, but had rejected it for what we must regard as a perfectly legitimate reason. ' At the time I formed the theory

of mixed gases,' he writes, ' I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygen gas contains just as many particles as the same volume of hydrogenous . . . but . . . I became convinced that different gases have *not* their particles the same size.'

The ground of his rejection of the hypothesis is as follows: ' It is evident that the number of ultimate particles . . . in a given weight or volume of one gas is not the same as in another; for if equal measures of azotic [nitrogen] and oxygenous gases were mixed, and could be instantly united chemically, they would form nearly two measures of nitrous gas [NO], having the same weight as the two original measures; but the number of ultimate particles could at most be one half of that before the union. No two elastic fluids, probably, therefore, have the same number of particles, either in the same volume or the same weight.'

DALTON was, in fact, inclined to believe that GAY-LUSSAC's experimental figures were inaccurate, and that the simplicity of his ratios was a deceptive one. His own results led him to think that ' gases do not unite in equal or exact measures in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments.' GAY-LUSSAC's results were, however, correct, and DALTON's were incorrect, so that the situation had reached an *impasse.*

Avogadro.—How the atomic theory was to be reconciled with GAY-LUSSAC's law could not be perceived by DALTON, simply and solely because the idea of the indivisibility of the atom had become an obsession with him. Thus, his biographer HENRY tells us that, to clinch a certain argument, he remarked with an air of finality: ' Thou knows IT MUST BE SO, for no man can *split an atom.*' It remained for AVOGADRO (1776–1856) to show how the reconciliation was to be effected, with no loss of honour or principle on either side.

AVOGADRO's supreme contribution to chemistry was his suggestion that a distinction might reasonably be made between the ultimate *chemical* particle of an element, the ' atom,' and the ultimate *physical* particle of a substance, the ' molecule.' While accepting the Daltonian indivisibility of the atom, he was able to visualize molecules of atomic dimensions which might or might not be divisible, according as they consisted of more than one atom or of a single atom.

In the light of this conception, he was able to offer an alternative hypothesis (1811) in explanation of GAY-LUSSAC's law. ' Let us,' he said, ' suppose that equal volumes of all gases—at the same temperature and pressure—contain equal numbers of *molecules.*'

'Setting out from this hypothesis,' he continues, 'it will be seen that we have a means of determining very easily the relative masses of the molecules of compounds which can be obtained in the gaseous state, and the relative number of these molecules in compounds; for the ratios of the masses of the molecules are then the same as those of the densities of the different gases, at equal pressure and temperature, and the relative number of molecules in a compound is given directly by the ratio of the volumes of the gases that form it. For example, since the numbers $1 \cdot 10359$ and $0 \cdot 07321$ express the densities of the two gases oxygen and hydrogen, taking that of atmospheric air as unity, and the ratio of these two numbers consequently represents the ratio between the masses of equal volumes of these two gases, it will also express, on the hypothesis suggested, the ratio of the masses of their molecules. Thus the mass of the molecule of oxygen will be about fifteen times that of the molecule of hydrogen, or, more exactly, $15 \cdot 074$ times. Similarly, the mass of the molecule of nitrogen will be to that of hydrogen as $0 \cdot 96913$ is to $0 \cdot 07321$, that is, 13 to 1, or more exactly $13 \cdot 238$ to 1. On the other hand, since we know that the ratio of the volumes of hydrogen to oxygen in the formation of water is 2 to 1, it follows that water results from the union of each molecule of oxygen with two molecules of hydrogen. Similarly, according to the proportions by volume established by M. Gay-Lussac in the elements of ammonia, oxide of nitrogen [nitrous oxide, N_2O], nitrous gas [nitric oxide, NO] and nitric acid [nitrogen peroxide, NO_2], ammonia will result from the union of one molecule of nitrogen with three of hydrogen, oxide of nitrogen from one molecule of oxygen with two of nitrogen, nitrous gas from one molecule of nitrogen with one of oxygen, and nitric acid from one of nitrogen with two of oxygen.'

The observation that DALTON found an insuperable obstacle to the acceptance of GAY-LUSSAC's law, viz. that one volume of nitrogen, if combined with one volume of oxygen, yields two volumes of nitric oxide, receives a simple explanation in terms of AVOGADRO's hypothesis. For if two volumes of nitric oxide are obtained from one volume of nitrogen and one volume of oxygen, then the plain fact is that each molecule of the last two gases must have been halved, and thus must consist of two atoms or of some higher even number.

With the clear distinction between atoms and molecules to assist them, chemists might have proceeded at once to the accurate and unequivocal determination of atomic and molecular weights, and might thus have entered fully equipped upon the investigation of molecular architecture. Unhappily, AVOGADRO's brilliant suggestion was neglected for nearly fifty years, partly owing the the fact

that he published it in a somewhat obscure journal, but mainly because DALTON's authority in theoretical chemistry was supreme and unchallenged. As a result of this neglect of AVOGADRO, confusion and bewilderment concerning atomic weights made formulae futile, and structural chemistry a subject for bitter conflicts over questions that were inherently impossible to settle. So hopeless did the whole position seem by the middle of the century that in 1860 a congress of chemists was summoned at Karlsruhe to consider the situation. LOTHAR MEYER, who was one of the members of the congress, relates that there he received a copy of a pamphlet by a young Italian named CANNIZZARO, and that on reading it he felt as though scales had been removed from his eyes: doubt vanished and was replaced by a feeling of serene security.

CANNIZZARO's pamphlet, entitled *Sketch of a Course of Chemical Philosophy*, was in effect a masterly demonstration of the use of AVOGADRO's hypothesis in settling the vexed question of atomic and molecular weights. He showed that the hypothesis enabled the relative weights of molecules of gases to be determined by the purely physical process of comparing the weights of equal volumes of those gases; and he further pointed out that, assuming the molecule of hydrogen to be diatomic (since the molecule of hydrogen chloride contains half a molecule of hydrogen), the molecular weights of gaseous substances must be twice their density referred to hydrogen.

'On the basis of the hypothesis [i.e. AVOGADRO's] cited above,' he says, 'the weights of the molecules are proportional to the densities of the substances in the gaseous state. If we wish the densities of vapours to express the weights of the molecules, it is expedient to refer them all to the density of a simple gas taken as unity, rather than to the weight of a mixture of two gases such as air.

'Hydrogen being the lightest gas, we may take it as the unit to which we refer the densities of other gaseous bodies, which in such a case express the weights of the molecules compared to the weight of the molecule of hydrogen=1.

'Since I prefer to take as common unit for the weights of the molecules and for their fractions, the weight of a half and not of a whole molecule of hydrogen, I therefore refer the densities of the various gaseous bodies to that of hydrogen=2. If the densities are referred to air=1, it is sufficient to multiply by 14·438 to change them to those referred to that of hydrogen=1; and by 28·87 to refer them to the density of hydrogen=2.

'I write the two series of numbers, expressing these weights in the following manner:

Names of Substances	Densities or weights of one volume, the volume of Hydrogen being made = 1, i.e. weights of the molecules referred to the weight of a whole molecule of Hydrogen taken as unity	Densities referred to that of Hydrogen = 2, i.e. weights of the molecules referred to the weight of half a molecule of Hydrogen taken as unity
Hydrogen	1	2
Oxygen, ordinary	16	32
Oxygen, electrized	64	128
Sulphur below 1000°	96	192
Sulphur above 1000°	32	64
Chlorine	35·5	71
Bromine	80	160
Arsenic	150	300
Mercury	100	200
Water	9	18
Hydrochloric acid	18·25	36·50
Acetic acid	30	60

'Whoever wishes to refer the densities to hydrogen=1, and the weights of the molecules to the weight of half a molecule of hydrogen, can say that the weights of the molecules are all represented by the weight of two volumes.

'I myself, however, for simplicity of exposition, prefer to refer the densities to that of hydrogen=2, and so the weights of the molecules are all represented by the weight of one volume.

'From the few examples contained in the table, I show that the same substance in its different allotropic states can have different molecular weights, without concealing the fact that the experimental data on which this conclusion is founded still require confirmation.' [Alembic Club Reprints, No. 18, pp. 6–7.]

CANNIZZARO next proceeded to establish the conception of the atomic weight of an element as the smallest weight of the element contained in the molecular weight of any of its compounds. Thus he showed that the weights of carbon in the molecular weights of the following compounds were all either 12 or a simple multiple of 12, whence he argued the atomic weight to be 12:

Compound	Molecular Weight	Weight of Carbon in Molecular Weight
Carbonic oxide	28	12
Carbonic acid	44	12
Carbon sulphide	76	12
Marsh gas	16	12
Ethylene	28	12 × 2
Propylene	42	12 × 3
Ether	74	12 × 4

Only a year after the congress of Karlsruhe, KEKULÉ was using vapour-density methods for determining the molecular weights of organic compounds; the atomic weights of carbon, sulphur, and oxygen were accepted to be 12, 32, and 16 instead of 6, 16, and 8; and the way lay open to that unhampered progress which marked the latter half of the nineteenth century. Then at length DALTON's atomic theory blazed into its full glory and rendered possible those amazing acquisitions of knowledge that were in due time to cause its own supersession.

Conclusion.—The main thread of the history of chemistry has now been carried up to the point at which, in such a book as this, the principal facts of later development may be more conveniently considered under the appropriate headings in the main portion. We have seen how empirical facts can be correlated and vivified under the influence of hypothesis and theory, and we have learned to appraise justly the value of each. Facts without theory do not constitute a science; theory without facts is an encumbrance and valueless. At bottom, a theory is no more than a succinct explanation: a concise description of the unfamiliar in terms of the familiar. When the description is found to be inadequate it must be modified, if modification will again render it adequate; otherwise it has to be abandoned and replaced by a better. Imagination therefore plays an important role in the progress of science, for the perception of the familiar in the apparently unfamiliar is only to be achieved by imaginative insight. Yet imagination must be controlled by constant reference to fact, by instant appeal to the laboratory: 'Let us learn to dream, gentlemen,' said KEKULÉ, 'then perhaps we shall learn the truth . . . but let us beware of publishing our dreams before they have been put to the proof by the waking understanding.' The elixir, the phlogiston, the hypostatical principle, the Daltonian atom, the ether, were all dreams that helped men in the eternal quest for truth, and have now passed into oblivion. We cannot doubt that the proton, the electron, and so forth are destined to suffer a similar doom, but history teaches us not to waste sentiment over the replacement of an outworn tool.

If then, Socrates, amid the many opinions about the gods and the generation of the universe, we are not able to give notions which are altogether and in every respect exact and consistent with one another, do not be surprised. Enough, if we adduce one as probable as any other. [PLATO, *Timaeus.*]

PART II

GENERAL AND THEORETICAL

CHAPTER I

ATOMS AND MOLECULES

The classification of matter—Elements—Mixtures and compounds—Definition of an element—Laws of quantitative chemistry—Dalton's atomic theory—Gay-Lussac's law of volumes—Avogadro's hypothesis—Exactitude of Avogadro's hypothesis—Atomic weights—Determination of atomic weights—Summary of atomic weight methods—Eudiometry—Molecular weights—Vapour-density determinations: Dumas' method, Hofmann's method, Victor Meyer's method—Glass spring tensimeters—Valency—Equivalents—The gravimetric composition of water—Richards' atomic weight work—Actual weight of atoms—Later development of the atomic theory.

The Classification of Matter.—Chemistry is concerned with the composition and behaviour of matter, and consequently with its classification. The simplest classification, into solids, liquids, and gases, more fully explored in the next chapter, though physical in kind, is of great significance for the chemist; but we shall first deal with a classification which led to the atomic theory of Dalton, and on which the whole structure of chemistry is based. [1]

Elements.—The idea of a pure substance was only vaguely understood early in the history of the science, and was not put into any very definite form until the nineteenth century, but early chemists would probably have agreed that indistinguishable samples of the same substance could be obtained from different sources. Before separation into the pure constituents takes place the conglomeration is called a mixture, and mixtures may be separated into their parts by such means as sublimation, distillation, or crystallization. Many of the pure substances thus isolated, which are perfectly homogeneous even under the microscope and which resist any attempt to decompose them made by such methods, can be further split up by the use of chemical reactions, yielding new pure substances that may perhaps be attacked in the same way; but a point will ultimately be reached at which further attempts at decomposition are fruitless. The resulting substance, which thus defies attempts to break it down into simpler substances, is called an element. The multiplicity of substances which compose the earth and its atmosphere is now known to result from the intercombinations of about ninety elements, of which about eight preponderate.

Mixtures and Compounds.—If an exhaustive study of a substance discloses circumstances, that, when they undergo continuous

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[1] The topics treated in the first few paragraphs of this chapter will be found more fully discussed in the Historical Introduction.

variation, cause corresponding continuous variation in the composition of the substance, then the material fails to qualify as a chemical compound, for which *fixity of composition* is to be taken as the most essential and fundamental property. A mixture of hydrogen chloride and water containing 20·22 per cent of the former boils under 760 mm. pressure constantly at 110° C., and the condensate is found to have the same composition as the original liquid. Further, the liquid is an active acid, a property not possessed by either of its constituents when separate. Such behaviour would suggest a compound, but when a further study showed that a continuous variation of the pressure occasioned not only a variation of boiling point, but also a continuous variation of the composition, it became clear that the liquid must be relegated to the category of mixtures (*see* p. 170). From aqueous solutions containing the salts potassium sulphate and ammonium sulphate in varying proportions, perfectly homogeneous crystals may be obtained, but with compositions varying in correspondence with that of the solution. On the other hand, when for ammonium sulphate aluminium sulphate is substituted, the salt potash-alum, containing a constant proportion of the two sulphates, is obtained from solutions of widely varying composition. On these grounds we say that the first example is a typical mixture, while the second is usually regarded as a compound (a double salt, p. 197). The progress of chemistry has shown that we can no longer hope to distinguish mixtures from compounds by reference to ' physical ' as distinct from ' chemical ' methods of attack. Heat will melt ice, and boil the water produced, and both these effects would commonly be termed ' physical ' changes. However, when the temperature is raised to the neighbourhood of 1000° C. the water undergoes the admittedly ' chemical ' change of dissociation into hydrogen and oxygen. To many chemists our present knowledge of the constitution of water suggests that its volatilization is quite as much a ' chemical ' as a ' physical ' change (see p. 103). Thus here the assignment of the same agency to physical or chemical roles is arbitrary. While it is probably true that the heat (or energy) changes involved in the more violent chemical actions are greater than those associated with so-called physical changes, and therefore that a large liberation of heat indicates *prima facie* a chemical change, a modern catalogue of heat changes would hardly allow a general distinction to be drawn that would be serviceable to distinguish the production of a mixture from that of a compound. Even the rigorous criterion of fixity of composition has suffered some relaxation since the discovery of isotopic elements. Contrary to Dalton's belief, we now have proof that the atoms of an element have not a constant single weight, but rather a range of weights. Thus, for example, there are two chemi-

cally indistinguishable atoms of lead, the one of atomic weight 206, and the other 208; and therefore the composition of lead monoxide may vary between the proportions 206/16 and 208/16 of lead to oxygen respectively.

Definition of an Element.—An element may be described as a substance which cannot by the ordinary methods of chemistry be decomposed into simpler substances. Since the beginning of the century this idea of an element has undergone modification. The former qualification, 'that has not yet been decomposed,' can now be dropped. It is quite true that many substances for long supposed to be elements were by the advance of chemical technique proved to be compounds, and when this was still possible such a qualification was very necessary. Since 1914, however, a criterion has been available (the X-ray spectrum, *see* p. 300) which allows us to decide beyond reasonable possibility of doubt whether a substance is an element or not, and we need consequently no longer adopt so diffident an attitude.

With modern resources the following succession of break-down processes is typical of what may be achieved with a substance such as water:

(1) Volatilization	Room temperature
(2) Dissociation to molecules of hydrogen and oxygen	Above 1000° C.
(3) Dissociation of molecules into atoms	Above 2000° C.
(4) Fission of atoms into simpler particles	Stellar temperatures.

Were these changes to be accomplished by purely thermal agency the temperatures required to secure a fair rate of change would be those indicated in the second column. In all the examples we might give of such a succession of decompositions there would be found an enormous gap between the intensities of attack required for stages (3) and (4). The sun's energy is almost certainly derived from the (indirect) condensation of four hydrogen atoms into one of helium, and we may gather from this the sort of intensity required to effect the reverse change. It is therefore natural and convenient at the present to separate 'ordinary' chemistry (corresponding to such changes as (1) to (3)) from what might well be termed 'stellar' chemistry, which is concerned with the break-up of elementary atoms and the re-combination of the parts. While the term *atom* is no longer literally justified, it is still true that most atoms are immensely more stable than the chemical compounds they form.

Laws of Quantitative Chemistry.—In the discussion of the differences between a mixture and a compound the *Law of Constant Proportions* has already been implicated. The discovery by PROUST

in 1797 of this law—for some years a matter of controversy—was only made possible by the enunciation by LAVOISIER of the *Law of Conservation of Mass*, which had served as a working generalization for chemists for many years previously, but first received definite confirmation from the experiments of the French chemist.

The most refined verifications were carried out by LANDOLT (1893–1908) and by MANLEY (1912). Landolt placed the reagents in the limbs of a glass H-tube, and mixed them by inverting the apparatus. After various sources of error had been eliminated, no difference in weight to 1 part in 10,000,000 could be detected before and after the reaction took place. For the reaction between sodium sulphate and barium chloride in aqueous solution Manley verified the law to 1 part in 100,000,000. Modern theory requires that reactions in which heat is given out should involve a slight decrease in mass, but the difference is far too small to be detected directly by any methods at the present available. Without the Law of Conservation of Mass gravimetric analysis is impossible, since the latter always depends on no matter being gained or lost. When once the Law of Constant Proportions was firmly established, analytical technique made great advances, and the *Law of Multiple Proportions* and that of *Reciprocal Proportions* quickly followed. The former states that when two elements combine in more than one proportion (by weight), then these proportions bear a simple ratio to one another; the latter that the proportions in which two elements separately combine with a third element are either in the ratio in which those two elements themselves combine or else in a simply related ratio. It was the consideration of these laws that in 1808 afforded JOHN DALTON support for the atomic theory which bears his name and which made possible the development of modern chemistry. A logical attitude to the laws of constant, multiple, and reciprocal proportions demands a definition of chemical combination, and of a chemical compound, independent of the laws. We have seen, however, that substances failing to exhibit constancy of composition are excluded from consideration as compounds. The law of constant proportions is thus in practice reduced to a truism.

Dalton's Atomic Theory.—The theory that matter consisted of discrete particles, based though it was rather on philosophical speculation than on experiment, had been a commonplace since the days of ancient Greece. Dalton himself seems to have been influenced chiefly by the views of NEWTON. The great contribution of Dalton—the essential buttress of his theory—was the application of gravimetric relationships to the problem of chemical combination. If the elements consisted of separate particles or atoms, then the compounds formed from them must consist of 'compound atoms' each of which contained atoms of the elements from which

it was derived. Since the weights of the elements present in these compound atoms were in a constant proportion, might not this proportion, in the simplest kind of compound atom (i.e. that of a binary compound), be simply the proportion of the weights of the atoms? If this were so, it was merely necessary to suppose that all the atoms of the same element were equal in weight for the Law of Constant Proportions to receive a natural explanation.

Dalton's theory may be summarized as follows:

(i) *Elements consist of indestructible atoms, all the atoms of the same element being exactly equal in weight and alike in all other respects.*

(ii) *Compound atoms are formed by the union of elementary atoms in simple numerical proportions; consequently the gravimetric composition of a compound is determined by the number of elementary atoms in the compound atom and by the atomic weights of the elements.*

The theory thus gave a satisfactory explanation of the Laws of Constant, Multiple, and Reciprocal Proportions; but at the end of the year 1808 GAY-LUSSAC published his *Law of Volumes*, and Dalton's theory found itself in difficulties.

Gay-Lussac's Law of Volumes.—Gay-Lussac's law, which was founded on his own researches, stated that the volumes in which gases combine bore a simple numerical relation to one another and to the volume of the product, if it were a gas, all volumes being measured at the same temperature and pressure. Gay-Lussac was content to state his experimental results without attempting their interpretation in the light of the new views of Dalton, but the connection between them could not fail to strike forcibly home to the chemists of the time. Gay-Lussac had shown that when gases combined their volumes were simply related, and Dalton considered that the numbers of combining atoms were simply related; it followed that there must be a simple relation between the numbers of atoms in equal volumes of the two gases. Let us suppose this simple relation to be an equality, equal volumes of all gases under similar conditions of temperature and pressure containing the same numbers of atoms, and let us apply this hypothesis to the combination of hydrogen and chlorine to form hydrogen chloride. Then since by experiment

1 volume hydrogen+1 volume chlorine=2 volumes hydrogen chloride,

it follows from our hypothesis that

1 atom hydrogen+1 atom chlorine=2 compound atoms hydrogen chloride.

*C

One compound atom of hydrogen chloride therefore contains only half an atom each of hydrogen and chlorine, which is contrary to Dalton's doctrine of the indivisibility of atoms. Similar contradictions are encountered in all gaseous reactions in which the volume of the gaseous product is greater than the volume of any one of the reactants.

The difficulty was a serious one, and Dalton probably had it in his mind when he denied the truth of Gay-Lussac's law. 'The truth is, I believe,' he wrote, 'that gases do not unite in equal or exact measures in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments' (see p. 51). There the matter rested till 1811, when AVOGADRO showed how the opposing views could be reconciled.

Avogadro's Hypothesis.—(An account of the development of the atomic and molecular theories will be found in the Historical Introduction.) Avogadro suggested that it was necessary to distinguish between the particles of gases and the atoms, or units, which took part in chemical change. In the elementary gases the atoms might be combined into larger units which he called *molecules*, each molecule containing some fixed number of atoms, frequently two. *Equal volumes of all gases under the same conditions of temperature and pressure contained equal numbers of molecules* (Avogadro's hypothesis). This idea circumvented the difficulty found in explaining the volume relations of hydrogen, chlorine, and hydrogen chloride, for if the molecules of hydrogen and chlorine each contained two atoms, and if one molecule of each gas combined to form two molecules of hydrogen chloride, then each molecule of the latter must contain one atom of each element: a satisfactory conclusion. Moreover some support was found for Avogadro's hypothesis from the coefficients of thermal expansion of gases, which under the same conditions of temperature and pressure are all equal; this shows that if the hypothesis be true at any temperature it must be true at all temperatures. Nevertheless this simple and ingenious supposition, which explained so much and against which no valid objection could be raised, had to wait half a century for recognition. Dalton's theory found an immediate if qualified acceptance, but Avogadro's hypothesis, which alone could bring it to its full usefulness, was generally neglected, and was strongly opposed by Dalton himself. The consequences of this neglect were most unfortunate for chemistry. From Dalton's theory alone it was impossible to deduce with any certainty a system of atomic weights. Dalton worked on the principle that when only one compound of two elements was known, it must be assumed to be binary; so he wrote the formula for water HO (hydrogen peroxide being as yet undiscovered), and this caused

error throughout the series. Confusion in the atomic weight table persisted right down to the time of CANNIZZARO, to whom the credit is due for finally securing general adherence to Avogadro's hypothesis in 1860. Since that day many eminent chemists have insisted that the hypothesis was a hypothesis still, but it has been universally adopted for the calculation of atomic weights, and in conjunction with Dalton's theory is the corner-stone of modern chemical theory. Since the development of the kinetic theory of gases and the theory of atomic number, independent methods of checking the hypothesis have been made available to science, and there is now no reasonable doubt that it gives a true picture of the facts. In particular, it has been found possible to calculate by several different methods the number of molecules in a gram-molecule of a gas at standard temperature and pressure (' Avogadro's Number '), and these calculations all agree within the degree of accuracy of the measurements.

Exactitude of Avogadro's Hypothesis.—Avogadro's hypothesis is not, however, one of the few generalizations (such as the Law of Conservation of Mass) which are obeyed with an accuracy greater than that of the experimental methods available for testing them. It is clearly dependent on the gas laws, and these, in their simplest form, are known to be only approximately true. In accurate deductions from Avogadro's hypothesis these small variations must be taken into account, and for this reason the vapour-density method is seldom used for the determination of molecular weights with great precision. It is, however, an almost indispensable preliminary to the determination of atomic weights by purely gravimetric methods, and the connection between the two processes must be briefly described.

ATOMIC WEIGHTS

The definition of *atomic weight* must first be discussed. The atomic weight of an element was originally defined as the ratio of the weight of an atom of that element to the weight of an atom of hydrogen. The atomic weight, defined in this way, is in fact not a weight at all, but a number. It was later pointed out that while only about half the elements formed compounds with hydrogen, nearly all formed compounds with oxygen, and that many of these compounds were very suitable for analysis. The atomic weight of oxygen on the hydrogen standard ($H=1$) is 15·875; it was therefore agreed that $O=16$ should be the standard: this makes hydrogen 1·008. A further advantage of the change is that with oxygen as standard other atomic weights approach more

nearly to whole numbers than with a hydrogen standard. This curious numerical relationship will be discussed in Chapter X. The choice of oxygen as a standard is complicated by the recent discovery that oxygen has isotopes (p. 321). If the pure isotope O^{16} is taken as standard, the almost constant minute amounts of O^{17} and O^{18} present in 'chemical' oxygen give the latter an apparent weight of 16·004: thus the difference between 'physical' and 'chemical' atomic weights is quite negligible for most purposes.

DETERMINATION OF ATOMIC WEIGHTS

1. We will suppose that the atomic weight of such an element as carbon is to be measured. A volatile compound containing carbon and only one other element must be selected and its vapour density determined, that is, the density compared with hydrogen=1 (at the same pressure and temperature). Methane will do very well; it is found to be eight times as dense as hydrogen. Since by Avogadro's hypothesis equal volumes of hydrogen and methane contain the same number of molecules, and since the hydrogen molecule is supposed to contain two atoms, the molecular weight of methane referred to H=1 must be 16. The atomic weight of carbon cannot, however, be calculated from this result without a knowledge of the number of atoms of carbon and hydrogen in the methane molecule. Gravimetric analysis shows that the ratio of carbon to hydrogen by weight in methane is as 3 to 1, or 12 to 4, so the simplest view would be that the atomic weight of carbon was 12 and the molecule of methane CH_4. We are, however, by no means justified in adopting this result without further inquiry, since the formula might equally well be C_2H_4, which would lead to an atomic weight of 6 for carbon; the atomic weight may indeed be 12 or any simple fraction of 12, but not more than 12. To decide between the possible formulae we must analyse and find the density of other volatile carbon compounds, tabulating the results as follows:

	Mol. wt.	Carbon		Mol. wt.	Carbon
Methane	16	12	Carbon monoxide	28	12
Ethylene	28	24	Carbon dioxide	44	12
Benzene	78	72	Carbon disulphide	76	12
Acetylene	26	24	Cyanogen	52	24

In no compound is it necessary to assume an atomic weight of less than 12 for carbon: we therefore provisionally accept this value.

2. DULONG and PETIT's *Specific Heat Law*, though it attracted no great attention for some time after its publication (1819), was

extensively used in the second half of the past century for the calculation, or rather the correction, of atomic weights. The law states that for the solid elements the product of the specific heat and the atomic weight is a constant (usually about 6). The following table gives an indication of the degree of exactitude of the law:

Element	Atomic Weight	Atomic Heat (20°–100°)	Element	Atomic Weight	Atomic Heat (20°–100°)
Al	27	5·9	Be	9	3·6–4·3
P	31	6·2	B	10·8	2·5–3·2
S	32	5·7	C (graphite)	12	2·0–2·8
Cu	63·6	6·0	(diamond)	12	1·4–2·2
Ag	108	6·1	Si	28	4·7–5·4
Pb	207	6·4			

Early opposition to the law was chiefly due to a conflict between atomic weights calculated from the law and those accepted at the time: later criticism has concentrated on the variation in the
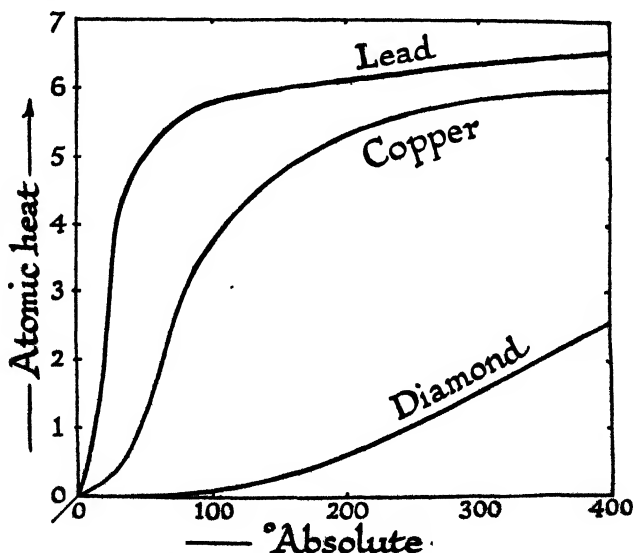
FIG. 2. VARIATION OF ATOMIC HEAT WITH TEMPERATURE

specific heats of the elements with temperature. Modern work at low temperatures has shown that the specific heats of all elements tend to zero as a limit as the temperature is reduced to the absolute zero, but that at high temperatures (different for each element) the

specific heat increases to a constant value in good agreement with the requirements of Dulong and Petit's law. The diagram (Fig. 2) shows the variation in the atomic heat (the specific heat at constant volume × the atomic weight) of lead, copper, and diamond between absolute zero and 400° Abs. The useful generalization of Dulong and Petit is no longer a scientific curiosity: it has received a satisfactory explanation on the basis of the quantum theory.

In order to determine the approximate atomic weight of a solid element it is therefore only necessary to measure the specific heat in a temperature range over which it is constant and to divide this figure into 6·4. This gives only an approximate value. Rather greater accuracy can be obtained by calculating the specific heat at constant volume by thermodynamical methods, and taking the atomic heat constant as 6·0. The exact figure must always be obtained by gravimetric analysis; in short, Dulong and Petit's law helps us to interpret the results of the analysis.

3. It is usually possible to come to conclusions about the atomicity of a gas (the number of atoms in the molecule) from measurements of the molecular heat at constant volume. For monatomic gases such as argon or mercury vapour this amounts to nearly 3 calories per gram-molecule, for diatomic gases the experimental values vary between about 4·7 and 6 calories, while for gases of higher atomicity the figures, though higher, are rather less constant. A physical interpretation of this relation can be given on the basis of the kinetic theory of gases (p. 100).

An approximate atomic weight for such an element as nitrogen can therefore be calculated from measurements of the density and specific heat at constant volume of nitrogen gas, and this can be combined with the results of analysis of the nitrogenous compounds ammonia or nitric oxide.

4. The method of chemical substitution is of interest because its results depend only on chemical methods and are independent of Avogadro's hypothesis. It may, however, easily lead to erroneous results, and in actual fact it appears never to have been used until the atomic weight had already been established by other methods.

Carbon is again the best example. Gravimetric analysis of methane shows it to consist of 3 parts of carbon to 1 of hydrogen. If now methane is exposed to the action of chlorine four substances can be isolated (methyl chloride, dichloromethane, chloroform, and carbon tetrachloride), in which one-quarter, one-half, three-quarters, and the whole of the hydrogen originally present in the methane has been replaced by chlorine. These proportions can be established by gravimetric analysis. Since the hydrogen can be replaced in four steps, four atoms of hydrogen must be present in the mole-

cule: the carbon, however, cannot be fractionally displaced, and is therefore present as a single atom. The formula for methane thus being found to be CH_4, the atomic weight of carbon must be 12.

5. The atomic weight can be estimated within a few units by assigning to the element on the basis of its properties and the properties of its compounds its proper place in the Periodic Table (Chapter X). The atomic weight of the rare element indium was found in this way in combination with the results of analysis. This method is entirely independent of Avogadro's hypothesis, and nowadays furnishes one of the strongest pieces of evidence of the truth of that hypothesis, but was naturally not available before the discovery of the Periodic Arrangement some eighty years ago. But long before this (in 1819) MITSCHERLICH discovered that compounds of similar but not identical composition crystallized in similar forms, and this phenomenon, which he named *isomorphism*, played some part in the original calculation of the atomic weights. Thus the chloride of the rare element rubidium is isomorphous with potassium chloride, and the molecule may therefore be expected to be of the same type: so that if potassium chloride is known to be KCl, then rubidium chloride is RbCl, and the atomic weight of rubidium can be calculated from the results of analysis.

6. The atomic weight can be directly calculated from the results obtained with the mass-spectrograph (Chapter X). Recent improvements in this instrument have greatly increased its accuracy, and it now rivals the analytical method for the determination of atomic weights. The results are independent of Avogadro's hypothesis, and give the true atomic weights, i.e. the atomic weights of the isotopes. If more than one isotope is present, then the relative proportions must be estimated before the ' chemical ' atomic weight can be calculated; this is difficult, but accurate results have been achieved.

Summary of Atomic Weight Methods.—We may summarize the available methods for the determination of atomic weights as follows:

Method	Experimental Data required	Law, Theory, or Hypothesis employed (in addition to Atomic Theory)
1.	Vapour density and gravimetric analysis of several compounds.	Avogadro's hypothesis.
2.	Specific heat of the element. Gravimetric analysis of a compound.	Dulong and Petit's law.
3.	Vapour density and specific heat at constant volume of gaseous element: gravimetric analysis of a compound.	Kinetic theory of gases. Avogadro's hypothesis.

Method	Experimental Data required	Law, Theory, or Hypothesis employed (in addition to Atomic Theory)
	Gravimetric analysis of compound and of substitution-products.	Doubtful train of reasoning.
5.	Study of properties of element and its compounds. }	Periodic law.
	Discovery of isomorphous compounds. }	Law of ison phism.
6.	Mass spectrum.	Fundamental laws of motion and electricity.

7.—Gravimetric analysis of gases is frequently a matter of great difficulty, but this process may be replaced by a volumetric study of suitable gas-reactions combined with Avogadro's hypothesis. Thus when equal volumes of hydrogen and chlorine combine there is scarcely any change in the volume of the system, and if hydrogen and chlorine can be shown to be diatomic—as they are—it follows immediately that the molecule of hydrogen chloride is HCl. The atomic weight of chlorine can then be accurately determined by gravimetric analysis of hydrogen chloride. The commonest example of this process is furnished by eudiometry, which can be used for any gas that forms an explosive mixture with oxygen. A eudiometer is simply a graduated barometer tube fitted at the top with a spark-gap between two platinum wires sealed through the glass. The gases to be studied are admitted separately while the tube is filled with mercury, and their volumes are measured and duly corrected for pressure and temperature. Reaction is then brought about by passing a spark, and when the resulting gas mixture has cooled its volume also is measured. The method is frequently applied to gaseous hydrocarbons, and it is then important to know what proportion of the products of combustion is carbon dioxide. This can be ascertained by passing a little concentrated potash solution up the tube, thus absorbing the carbon dioxide while leaving the other gases unchanged. Unless the eudiometer is surrounded by a vapour-jacket, the water produced by the combustion of substances containing hydrogen will be condensed to a liquid, whose vapour-pressure must, however, be allowed for, even if its volume is negligible in comparison with that of the gases.

The principle of the instrument may be made clear by the following example, an experiment to determine the formula of the gaseous hydrocarbon methane. All volumes have been reduced to N.T.P.

15·7 c.c. of methane and 40·2 c.c. of oxygen were introduced

into the eudiometer and a spark was passed, the methane being oxidized to carbon dioxide and water according to the equation

$$C_xH_y+(x+\frac{y}{4})O_2=xCO_2+\frac{y}{2}H_2O.$$
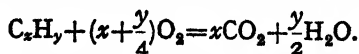
The volume of the carbon dioxide produced and of the unused oxygen amounted in all to 24·5 c.c., the water being present as a liquid and the whole of the methane having been consumed. The carbon dioxide was absorbed by potash and the residual oxygen was found to occupy a volume of 8·8 c.c., that of the carbon dioxide having been therefore 24·5—8·8=15·7 c.c., that is, equal to the original volume of the methane. It follows that $x=1$, and since the volume of oxygen consumed, 40·2—8·8=31·4 c.c., was twice the original volume of methane, $x+\frac{y}{4}=2$, or $y=4$. The formula of methane is therefore CH_4.

MOLECULAR WEIGHTS

The methods for the determination of the *molecular weight* of a substance may be divided into two classes:

  (i) *Measurements of the vapour density.*
  (ii) *Measurements of the molecular weight in solution,* based on the properties such as vapour pressure, freezing- and boiling-points which are related to the osmotic pressure of the solution. These are discussed in Chapter IV.

Not all compounds can be vaporized at a temperature low enough to make determinations by the first method possible, but it should be clearly understood that the two methods do not always measure the same thing, as the molecular weight in solution may not be the same—and for a large class of substances is not the same—as the molecular weight in the vapour phase (see Chapter IV). It is also dangerous to assume that the molecular weight in the vapour phase corresponds with the simplest possible formula, since both association into double or more complicated molecules and dissociation into other compounds or into atoms are possibilities to be reckoned with. As to the molecular weight in the solid state, it has not been possible to investigate it at all until recent years, and our knowledge of the subject is still far from general. The molecular weight of pure liquids is also a subject on which little precise information is available. These subjects are discussed in the next chapter.

Vapour-Density Determinations.—Apart from researches of high precision, in which special methods are always used, there are three

methods commonly employed in the laboratory to measure the density of a vapour. The object of all these methods is to measure the volume of a known mass of vapour at a known temperature and pressure.

1. *Dumas' Method.*—A small quantity of the liquid is introduced into a weighed glass bulb, drawn out at one end into a long thin-walled capillary tube (Fig. 3). The bulb is then placed in a thermostat at a temperature high enough to make the liquid boil vigorously. At high temperatures a constant-temperature air bath can be substituted for the thermostat. As soon as all the liquid in the bulb has vaporized, that is, as soon as vapour ceases to stream from the bulb, the capillary tube is sealed off, and the bulb is cooled and weighed. The volume occupied by the vapour is then found by opening the tip of the capillary tube under water free from dissolved air and weighing the bulb with the water which rushes into it, but if this water does not fill the bulb, not all the air was expelled from it during ebullition, and the experiment must be repeated. The calculation offers no difficulty, and will be made clear by an example.

FIG. 3. VAPOUR DENSITY BY DUMAS' METHOD

An experiment was carried out with benzene at 100°, and it was found that at this temperature, and at a barometric pressure of 754 mm., 115·7 c.c. of benzene vapour weighed 0·293 gm., all weights having been reduced to vacuum. The density of benzene vapour at N.T.P. is therefore $\dfrac{0\cdot293 \times 1000 \times 760 \times (273 + 100)}{115\cdot7 \times 754 \times 273}$

=3·507 gm. per litre. But the density of hydrogen at N.T.P. is 0·0899 gm. per litre, so the vapour density of benzene (H=1) is $\dfrac{3\cdot507}{0\cdot0899}$=39. Since the molecular weight of hydrogen is 2, the molecular weight of benzene is 2×39=78.

2. *Hofmann's Method.*—In this method a known weight of a volatile liquid, enclosed in a small bulb which it must fill completely, is introduced into the vacuum above the mercury in a barometer. The barometer tube is usually enclosed in a steam-jacket (Fig. 4), and the bulb is allowed to float up to the surface of the mercury, where the internal pressure is sufficient to expel the stopper. The

barometer tube is graduated from the top, and when the mercury is steady the volume, temperature, and pressure of the vapour can be read.

3. *Victor Meyer's Method.*—In this method we measure the volume of air displaced by a known weight of a volatile liquid in vaporizing. Various devices can be used to measure the volume at atmospheric pressure, perhaps the best being that shown in the
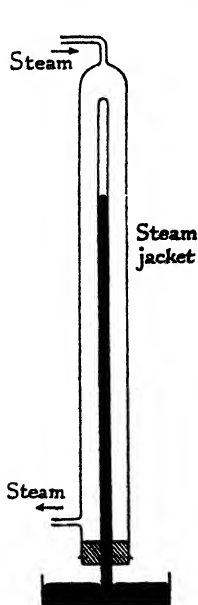
FIG. 4. VAPOUR DENSITY BY HOF-MANN'S METHOD
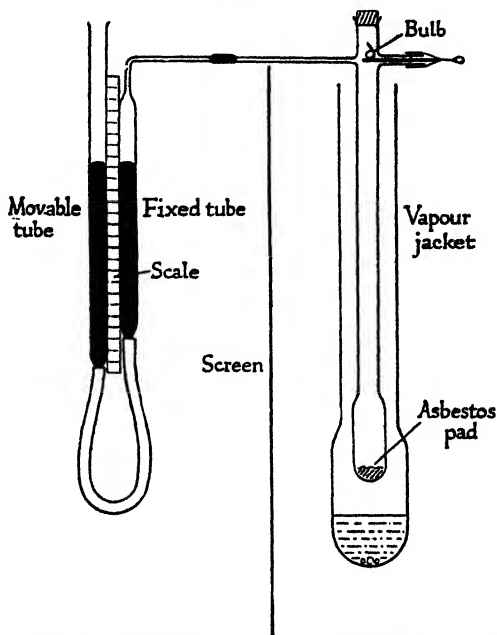
FIG. 5. VAPOUR DENSITY BY VICTOR MEYER'S METHOD

diagram (Fig. 5). The weighed bulb is placed on the movable support in the top of the apparatus, the bung is inserted, and the mercury levelled in the two tubes while the liquid in the vapour-jacket is boiled briskly. When the mercury levels are steady the bulb is allowed to fall to the bottom of the tube, where the contents are vaporized, the base of the tube being protected by an asbestos pad. The mercury is again levelled, and the volume of air displaced is read at room temperature and pressure. The volume actually measured is the volume the vapour would have at the temperature of the room, since we are entitled to assume that it has the same coefficient of expansion as the air that it displaces, and

the increase in volume of the gas in the apparatus takes place in the colder part of it.

Example:

0·1743 gm. of carbon tetrachloride was vaporized (in a steam-jacket), and the volume of air displaced was 26·7 c.c.   The temperature of the tubes containing mercury was 12°, and atmospheric pressure was 748 mm.   The volume of the carbon tetrachloride vapour at N.T.P. was therefore $\dfrac{26\cdot7\times273\times748}{(273+12)\times760}$ c.c., and the weight of a litre of the vapour at N.T.P. is

$$\dfrac{0\cdot1743\times1000\times(273+12)\times760}{26\cdot7\times273\times748}\ \text{gm.}=6\cdot923\ \text{gm.}$$

FIG. 6.   GLASS SPRING TENSIMETER

But a litre of hydrogen at N.T.P. weighs 0·0899 gm., so the vapour density of carbon tetrachloride (H=1) is $\dfrac{6\cdot923}{0\cdot0899}=77$.   The molecular weight of carbon tetrachloride is therefore $2\times77=154$.

In Victor Meyer's apparatus the vapour of the substance under examination is diluted with air.   The molecular weight of certain substances (p. 414) will be affected by this dilution, and for such substances the methods of Dumas and Hofmann are to be preferred.   Apart from this possibility of association or dissociation of the vapour, the method of Victor Meyer, though rapid and convenient, does not give results of a high order of accuracy.

Glass Spring Tensimeters.—For modern precise determinations a glass spring tensimeter is commonly used (Fig. 6).   A weighed quantity of the substance is introduced into the bulb A, the air is exhausted, and the tube B sealed up.   A is connected to a glass membrane C attached to a pointer D, which sometimes carries a small mirror, so that very slight movements can be detected by the reflection method used in mirror galvanometers.   The outside of the glass membrane is enclosed in a chamber connected to a pump and manometer.

The bulb A, whose volume must be measured in a separate experiment, is raised to a constant and accurately known tempera-

ture. Any difference of pressure between the inside and outside of the glass spring causes the glass to bend and the pointer to move. The pump is therefore worked until the pointer is brought back to the position corresponding with zero pressure difference, and the external pressure (which must now be equal to the internal pressure) read off on the manometer. The mass, volume, temperature, and pressure of the vapour are then all known.

The membrane is sometimes replaced by a spiral tube of elliptical section, which tends to uncoil when the internal pressure is increased. With a quartz apparatus the measurements can be carried above the melting-point of glass.

Valency.—Since different atoms combine with different numbers of hydrogen atoms, a term is needed to express this number. It is called the *valency*, and may be defined as the number of hydrogen atoms which combine with an atom of the element. This definition embodies a true conception of valency as representing the extent to which combining power may be subdivided, but is incomplete, and in particular fails to cover such examples as SH_2 and SF_6 in which the univalent element fluorine evokes in sulphur a higher valency than hydrogen does. A discussion of valency will be found in Chapter XI.

EQUIVALENTS

The equivalent of an element is the number of units of weight of it which will combine with or replace one of the same units of weight of hydrogen. This definition is based on the hydrogen standard of atomic weights; on the oxygen standard the equivalent is the number of units of weight which will combine with or replace 8 units of weight of oxygen. From this definition it is easy to see that the equivalent is equal to the atomic weight divided by a small integer, which will frequently be equal to the valency, but is not necessarily so; a consideration of the stable compounds, ammonia NH_3, nitrous oxide N_2O, and nitric oxide NO, will illustrate this matter.

The Gravimetric Composition of Water.—The direct determination of the combining weights of oxygen and hydrogen is a matter requiring the highest experimental skill, since the weight of all gases, and especially of hydrogen, is so small in comparison with that of the vessel containing them. The determinations of MORLEY (1895) have since become classical. Morley weighed the water obtained by the combination of a known weight of hydrogen and oxygen. The combustion took place in a glass apparatus (Fig. 7) which could be weighed on the balance. The carefully dried and purified gases were contained in large weighed globes, and were admitted to the central tube through platinum jets. During the

combustion an excess of oxygen was maintained, and the hydrogen, ignited by a spark between the sealed-in platinum wires, burned quietly at the jet while the apparatus was cooled to condense the water produced. Finally the apparatus was cooled in a freezing-mixture while the residual gas was pumped off, analysed, and weighed. Any water-vapour carried by the issuing gas was retained by the phosphoric oxide through which it had to pass. After the removal of the gas the apparatus was weighed, and the weight of water calculated by difference. A check on the results is provided by the total weight of the hydrogen and oxygen consumed, since this must be equal, within the experimental error, to the weight of the water produced. The result of the experiments was a value 7·9396 for the equivalent of oxygen.

The equivalent of any other element can be calculated directly from the results of the gravimetric analysis of its oxide or hydride. If the analysis of these compounds is inconvenient, any others may be used provided that they contain, in addition to the element whose equivalent is to be determined, only elements whose equivalents are already known. An example from the work of RICHARDS will make this clear. Richards, who was Professor of Chemistry at Harvard University, carried the precision of chemical analysis to a point previously unknown, and in a crowded life determined the atomic weights of nearly all the important elements. In one well-known series of experiments he found that 100·000 gm. of the purest silver yielded 132·867 gm. of silver chloride, which therefore contained 32·867 gm. of chlorine. Since the equivalent of silver was found from other experiments to be 107·920, the equivalent of chlorine was $32·867 \times \dfrac{107·920}{100·000} = 35·470$. It was also

Hydrogen   Oxygen

Phosphoric oxide   Phosphoric oxide

Platinum jets

FIG. 7. MORLEY'S SYNTHESIS OF WATER

known that both silver and chlorine are univalent, so these numbers, 107·920 and 35·470, represented their atomic weights as well as their equivalents.

Richards' Atomic Weight Work.—A brief account of one of Richards' atomic weight determinations is given in the section on nitrogen (p. 425). A fascinating summary of his life and work will be found in the Richards Memorial Lecture (printed in the *Journal of the Chemical Society*, 1930), and every student should read, if possible, his short essay on *Methods used in Precise Chemical Investigations*, into which he condensed the experience of a lifetime of successful research. A few leading principles may be mentioned here.

He begins by emphasizing the importance of measuring atomic weights with the utmost attainable accuracy. No better example of this can be given than the slight variation from unity of the atomic weight of hydrogen (1·0080) on the oxygen standard; this variation has been made the starting-point for most important deductions as to the nature of the atomic nucleus (Chapter X). The choice of material for an atomic weight determination must be governed by the following considerations:

(i) The compound selected must be capable of preparation in a state of great purity.

(ii) The other elements contained in it must be of known atomic weight.

(iii) It must be capable of exact analysis or synthesis without loss of material.

Of all the difficulties of such work, that of purity is perhaps the most insistent. Solids separating from the vapour phase or from a solution always carry with them some part of any impurity which may be present, and the effort to overcome this effect led Richards to some of his most important improvements in method:

(i) The use of a centrifuge or whirling machine to free crystals from mother liquor.

(ii) The study of *occlusion*, that is, the tendency of precipitates to carry down with them other substances present in solution. Even hard, shining crystals of electrolytically precipitated silver were found to contain solution enmeshed within invisible cavities in the solid.

(iii) The bottling apparatus (illustrated on p. 426), in which substances can be heated in any desired gas or in a vacuum, and weighed without exposure to the air.

The solubility of all so-called 'insoluble' substances in contact with the solutions must be carefully studied. Glass is not completely unaffected by water, and this led to the presence of silica

in most of the preparations of previous workers; Richards used vessels made from platinum or fused quartz. If such a substance as silver chloride is to be precipitated, its solubility in water must be estimated and allowed for; for this purpose Richards developed the nephelometer (p. 427). Traces of solid are easily carried away when solutions are evaporated to dryness, and to avoid this loss the conditions of evaporation must be carefully devised, and controlled by blank experiments. Substances must be protected from dust by the use of hoods and enclosed vessels, and heating by coal-gas, which leads to contamination by impurities present in the gas, must be replaced by electrical heating. 'Every substance must be assumed to be impure, every reaction must be assumed to be incomplete, every method of measurement must be assumed to contain some constant error, until proof to the contrary can be obtained. As little as possible must be taken for granted.'

Actual Weight of Atoms.—To calculate the true weight of an atom from the atomic weight we require to know the weight of an atom of hydrogen, or alternatively a knowledge of Avogadro's number N will do as well. This constant has been calculated by a variety of physical methods into which we cannot enter here. The remarkable concordance of the results is shown very strikingly in the table.

Phenomenon observed	$N \times 10^{-23}$
Brownian movement:	
Distribution of particles (1909) .	6·09
Diffusion of particles (1912) . .	6·08
Black body spectrum (1900) . .	6·03
Radioactivity (counting particles, 1908)	6·04
Electronic charge (1910) . . .	6·03
Crystal structure (1922)	6·02

Some account of the measurements included under the heading 'Brownian movement' will be found in Chapter IX. The best value of N is probably $6·023 \times 10^{23}$. Since a gram-molecule of hydrogen weighs almost exactly 2 grams, the weight of an atom of hydrogen is $1·66 \times 10^{-24}$ grams.

Later Development of the Atomic Theory.—In the face of the evidence for the atomic structure of matter summarized in this chapter and in the next, no theory involving a continuous structure for matter could nowadays receive serious attention. There are, however, two tenets of the atomic theory, as commonly accepted in the nineteenth century, for which we have as yet adduced no evidence—the doctrines that atoms are indestructible and that all atoms of the same element have the same weight. The first

doctrine was shown to be untrue by the development of the theory of radioactive disintegration, the second was disproved by ASTON with the help of the mass-spectograph. The consequences of this development are further discussed under the heading of isotopes, p. 312.

SUGGESTED FOR FURTHER READING

See the short bibliography on p. 56.

HARTLEY: *T. W. Richards*, Memorial Lecture Chem. Soc. 1929.

WHYTELAW-GRAY: 'Limiting Densities,' *Chem. Soc. Quart. Rev. 4.*

GIBSON: 'Terrestrial Distribution of the Elements,' *Chem. Soc. Quart. Rev. 3.*

BERRY: *Modern Chemistry.*

CHAPTER II

THE STRUCTURE OF MATTER

Solids, liquids, and gases: SOLIDS—Crystals and undercooled liquids—Crystal angles—Internal structure of crystals—Laue's experiment—Ionization in crystals — Methods of structural analysis — Crystal structures — Ionic diameters—Liquid crystals. GASES—Kinetic theory of gases—Distribution of molecular velocities—Kinetic theory and the gas laws—Imperfect gases—Liquefaction of gases—Diffusion—Dalton's law of partial pressures — Thermal conductivity — Specific heats — Viscosity. LIQUIDS — Pure liquids—Molecular weight and association—The parachor—Characteristics of associated liquids—Films of polar molecules

Solids, Liquids, and Gases.—In this chapter we shall consider the solid, liquid, and gaseous states of matter from the point of view of structure rather than of chemical behaviour. Though most of the experiments on which our knowledge of this part of science is based have been made by physicists, an acquaintance with their results is of the highest importance to chemists, upon many of whose problems they have cast new light. We saw in the previous chapter how essential a part the study of gases played in the beginnings of the atomic and molecular theories. This study has been pursued continuously since the eighteenth century and is still yielding valuable results, but the peculiar contribution of the present century to these theories, apart from the phenomena of radioactivity, has been derived from the study of crystalline solids. Compared with our knowledge of gases and solids, our ideas of the liquid state are still very vague, and progress is still slow. In the solid the atoms or molecules are held strictly in position by the cohesive forces between them, and the consequent regular arrangement can be observed. In gases the molecules are separated by distances over which the attractive forces are scarcely operative, but the number of molecules is so great that the complete disorder in which they move can be investigated with high accuracy by statistical methods. In liquids, on the other hand, the cohesive forces are insufficiently strong to maintain a regular arrangement of molecules in the interior of the substance, but are strong enough to prevent any rapid escape of molecules from the surface. Our ignorance of the laws that govern these cohesive forces has left us very much in the dark as to the nature of the liquid state, though of surface phenomena we now have some slight knowledge.

SOLIDS

Crystals and Undercooled Liquids.—The large majority of solids, whether natural or artificial, are definitely crystalline: that is to say, they are either of regular shape or can be resolved into smaller (if necessary, microscopic) particles of regular shape. Such substances as glass or resin which show no regular structure are not true solids, but undercooled liquids; that is, liquids in course of crystallization so slow that over ordinary periods of time it cannot be observed. The condition of an undercooled liquid is then, strictly speaking, unstable, and is liable to change spontaneously into the crystalline condition. This is well seen in old soda glass, which on strong heating sometimes ' devitrifies,' and in a few seconds becomes a mass of small crystals no longer fluid at that temperature.

Potassium perchlorate
$K Cl O_4$

Copper sulphate
$Cu SO_4 \cdot 5 H_2O$

Calcium carbonate
(Aragonite),$CaCO_3$
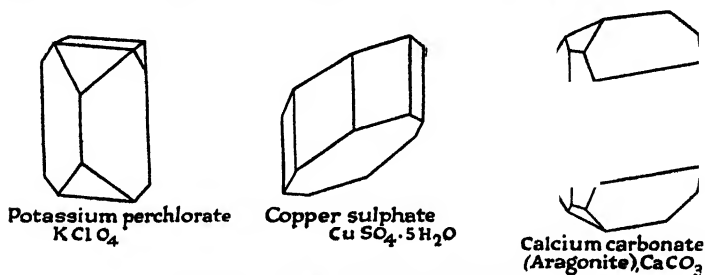
FIG. 8.   SOME PERFECT CRYSTALS

Crystal Angles.—The study of crystals is as old as the study of science, and for many years we have been in possession of accurate measurements of the regular shapes in which crystalline substances occur. Natural crystals are seldom perfectly regular, but by cleavage or splitting they can be reduced to perfect forms of the same shape though not necessarily of the same size. The diagram (Fig. 8) shows some perfect crystals. The same chemical individual always crystallizes in the same shapes, the majority having only one crystalline form, others two or more. Crystalline form is not examined by measuring the lengths of the edges, but by measuring the angles between the faces; in this way a description of the form of the crystal can be given which is quite independent of size.
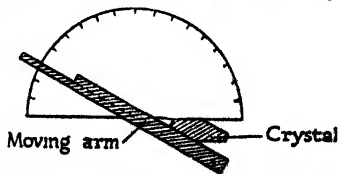
Moving arm

Crystal

FIG. 9.   CONTACT GONIOMETER

The instrument with which the angles are measured is called a *goniometer*. In the old or contact form of the instrument the crystal was held between a rigid plate and a rotating arm moving

over a scale graduated in degrees. In modern instruments we measure the angle through which the crystal must be turned to bring into a telescope the same ray of light reflected from the faces in turn. By a succession of such measurements the angles between all the faces can be found. These angles are the same for similar crystals of the same substance, but it is usually more convenient to record the ratios of the intercepts which planes parallel to the faces would make on three axes in space. Axes usually taken parallel to three prominent edges of the crystal; ey need not be at right angles, but they must me at a point. In the ram (Fig. 10) OX, OY, and OZ have been taken as axes, and a plane has been drawn making intercepts OA, OB, and OC on these axes. If the plane DEF, making intercepts OD, OE, and OF, is parallel to the plane ABC, it follows from simple geometry that the ratio OA : OB : OC is equal to the ratio OD : OE : OF. Further, the ratio can
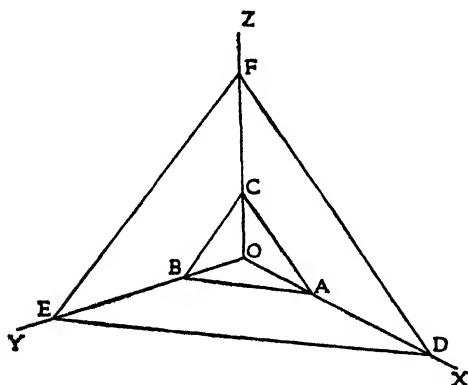
FIG. 10.   INTERCEPTS ON AXES

be simplified by making any one of the intercepts equal to unity and altering the others in proportion. Since similarity of crystalline form means neither more nor less than parallelism of the faces when the crystals are in corresponding positions, it follows that crystalline form can be recorded by a set of such ratios, though not every pair of similar crystals may have all the corresponding faces present. Alteration of the relative sizes of the faces may produce great differences in appearance in a pair of similar crystals, but the goniometer brings these differences into coincidence. It is also found that for the same crystal and the same axes the intercept ratios of the different faces bear simple relations to each other. With the help of these relationships crystals have been divided into a number of systems expressing differences of form, such as the *cubic*, the *rhombohedral*, the *triclinic*, the *monoclinic*. This classification is still necessary to the worker in this field, but since the discovery of X-ray methods of crystal analysis it has become more useful to concentrate attention on the more intimate structures which the crystal has been made to reveal.

Internal Structure of Crystals.—Many years ago it was surmised

that the external regularity of crystals was due to a regular internal arrangement of minute structural units often compared to bricks, and by some it was supposed that these structural units were no other than molecules. These ideas were developed by the ABBÉ HAÜY (1743–1822), who showed them to be in accordance with the known properties of crystals. The units need not have plane faces like bricks; they may also be thought of as spheres in regular arrangement such as exists in a pile of cannon-balls. These views found general acceptance, but it was scarcely possible, except in the vaguest terms, to discuss the relation between the shape of the molecule and the shape of the crystal until a historic experiment suggested by LAUE began a new era in crystallography.

With the investigation of radioactivity and the elucidation of atomic number this ranks among the greatest advances of twentieth-century chemistry, and of these advances two were made with X-rays. Scientific progress is cumulative; every advance in pure science is valuable not only in itself but in the assistance it gives to other branches.

From 1895, when X-rays were discovered by RÖNTGEN, evidence had been slowly collected that X-rays were radiation differing from light only in their very much smaller wave-length. Attempts had been made to measure this wave-length by means of diffraction, a method familiar to students of physics, but the finest slits which could be constructed were found to be too wide for the purpose. Improvements were made in technique, and in the spring of 1912 SOMMERFELD was able to estimate the wave-length to be of the order of 4×10^{-9} cm., a result not very far from the truth.

Laue's Experiment.—In the same year it occurred to Laue that since the wave-length of X-rays appeared to be rather less than the distance to be expected between the structural units of a crystal, it should be possible to obtain a diffraction pattern by passing a beam of X-rays through a thin crystal section. The experiment was carried out according to his suggestions by FRIED-RICH and KNIPPING at Munich and was a brilliant success. The photographic plate on which the X-rays were allowed to impinge after passing through the crystal was found to be covered with a symmetrical arrangement of spots about a large central patch due to the undeviated part of the X-ray beam. This experiment had two results of the greatest importance: on the one hand it made it possible to calculate with ease and precision the wave-length of any given beam of X-rays, on the other it was the beginning of our definite knowledge of the internal structure of crystals. Fig. 11 shows Laue photographs of beryl ($3BeO$, Al_2O_3, $6SiO_2$) and nickel sulphate.

Since 1912 the photographic method of Laue has been supplemented

and to some extent replaced by other methods. We shall first discuss the theoretical basis of the reflection method developed by SIR WILLIAM BRAGG and his son, now SIR LAWRENCE BRAGG.
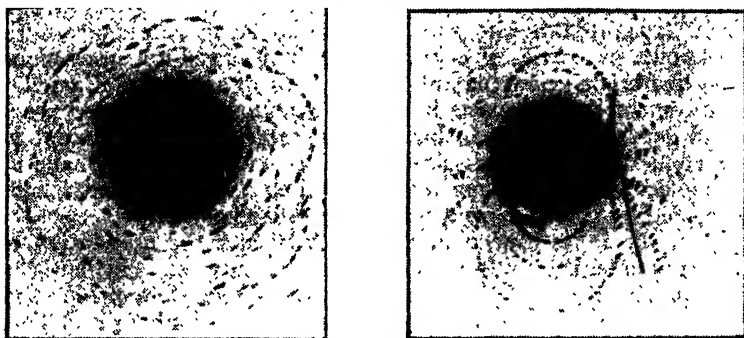
By permission of Sir William Bragg and the Royal Society
FIG. 11.   LAUE PHOTOGRAPHS: BERYL, NICKEL SULPHATE

Consider a beam of X-rays all of the same wave-length (and hence called monochromatic by analogy with light) reflected from a crystal, bounded by the plane LM, in which the structural units form layers PQ, RS, etc.   Let A and B be two parallel rays in the beam, meeting LM and PQ at V and X respectively, where VX is normal to the surface, and let θ be the glancing angle (the complement of the angle of incidence of optics), and let the distance VX, that is, the distance between the layers, which are evenly spaced,
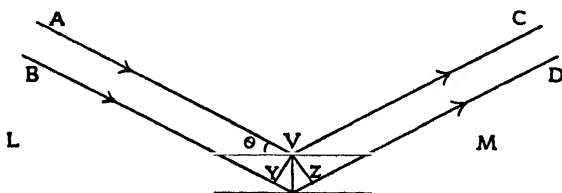
FIG. 12.   DIFFRACTION OF X-RAYS

be denoted by d. Then the waves in the reflected ray D will lag behind the waves in the reflected ray C by the extra distance which the ray B has had to travel, that is, by the distance XY+XZ, VY and VZ being perpendicular to B and D respectively.   Since the angle YVX and the angle ZVX are both equal to θ, this distance amounts to $2d \sin \theta$.   If this distance is equal to any whole number of wave-lengths, the rays C and D will form part of a bright beam

of X-rays, but if it is not, the difference in phase between parallel rays will produce ' darkness.' The reflected X-rays are therefore collected in a number of narrow beams over a blank field, and this is the explanation of the dark spots in the Laue photographs, each dark spot on the negative corresponding with an X-ray beam. It is clearly immaterial whether the X-rays are reflected from the surface layers or are passed through a thin crystal section; in either case the angle θ which a ray producing a bright beam forms with the internal layers must obey the equation $n\lambda = 2d \sin \theta$, where n is a whole number and λ the wave-length; d can then be calculated from λ and θ.
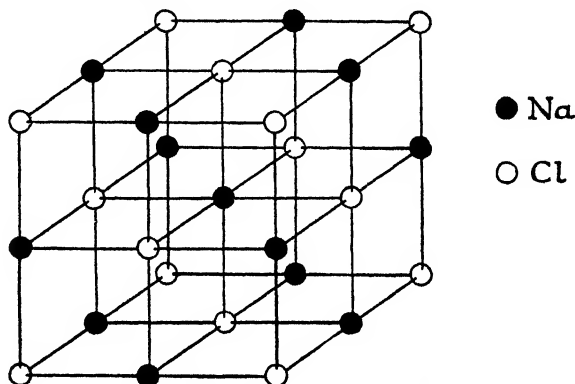
FIG. 13. THE STRUCTURE OF SODIUM CHLORIDE

Among the earliest crystals to be investigated were the isomorphous sodium and potassium chlorides. It was found that the crystal of sodium chloride, which is cubic, contained three sets of parallel layers at right angles to each other, each layer being separated from its neighbours by $5\cdot63 \times 10^{-8}$ cm. The volume of the cubes contained between these layers was therefore $(5\cdot63 \times 10^{-8})^3$ $= 1\cdot78 \times 10^{-22}$ c.c. Since the density of sodium chloride is $2\cdot17$ gm. per c.c. the mass contained in this unit cube was $2\cdot17 \times 1\cdot78 \times 10^{-22}$ gm. $= 3\cdot87 \times 10^{-22}$ gm. The molecular weight of sodium chloride is $58\cdot5$, and the mass of the hydrogen atom $1\cdot66 \times 10^{-24}$ gm., so the mass of a molecule of sodium chloride is $0\cdot973 \times 10^{-22}$ gm. The unit cube therefore contains $\dfrac{3\cdot87 \times 10^{-22}}{0\cdot973 \times 10^{-22}} = 4$ molecules of sodium chloride. Similar results can be obtained for potassium chloride. It remains to be seen how these molecules or atoms are to be arranged within the cube.

It is known that the absorption of X-rays by matter is roughly

proportional, for equal numbers of atoms, to the atomic number: it is therefore not unreasonable to suppose that the reflection of X-rays varies in a like manner. By a study of the intensity of the reflected beams it is then possible to place the atoms with some certainty: for in potassium chloride the atomic numbers of the two atoms are very roughly equal, whereas in sodium chloride they differ considerably. The structure of the unit cube arrived at in this way is shown in Fig. 13, the black dots representing sodium (or potassium) atoms, the white ones chlorine atoms.

Several interesting points are at once obvious in the diagram. In the first place, it appears to contain 27 atoms, whereas the unit cube contains only four molecules, or eight atoms. It must, how-ever, be remembered that the unit represented is only one of a number of contiguous cubes. The corner atoms are to be shared between eight cubes, and therefore count only one-eighth each, the atoms on the edges count one-quarter, and the atoms on the centres of the faces count one - half. In the second place, the molecule has disappeared: there remain only atoms. Each chlorine atom has six sodium atoms for its nearest neighbours, but as they are equidistant it is no more closely connected with any one than with any other, and each sodium atom is surrounded by six chlorine atoms. This can be most clearly seen at the central sodium atom; for the others the contiguous cubes must not be forgotten. Indeed in all questions of crystal structure it is highly important, when drawing any conclusions from a diagram of the crystal unit, to remember that it is one of a series extending in three dimensions.

Ionization in Crystals.—The question inevitably arises: Are we expected to believe that the atoms of sodium and chlorine thus brought into very close companionship are the same atoms to which in the elementary state such violent affinity for each other is attri-buted? And how can a regular arrangement of sodium and chlorine atoms in space constitute a compound whose properties in no way resemble those of its elements? The answers to these questions cannot be fully understood till the modern electron theory of chemical combination has been discussed, but in the meantime it may be stated that independent studies of the physical properties of salt crystals have conclusively proved that the particles present in the crystal structure are not atoms such as exist in the element but bodies called *ions*, consisting of sodium and chlorine atoms whose chemical properties have been entirely altered by the exchange of an electric charge. It is these acquired electric charges that hold the ions in position in the crystal structure; the negatively-charged chlorine ion is securely held in place by the six positively-charged sodium ions which surround it.

Methods of Structural Analysis.—We may now briefly describe

the principal methods by which these results are achieved. In the Laue method the monochromatic X-rays, narrowed to a fine pencil by passage through a lead diaphragm, pass through a thin slice of the crystal and are received on a photographic plate on which the central undeviated ray falls normally. The Braggs altered this method in two particulars: they reflected the rays from the crystal, which was mounted on a turntable, and they determined the angles at which intense reflection occurred by passing the reflected ray into an ionization chamber. X-rays have the property
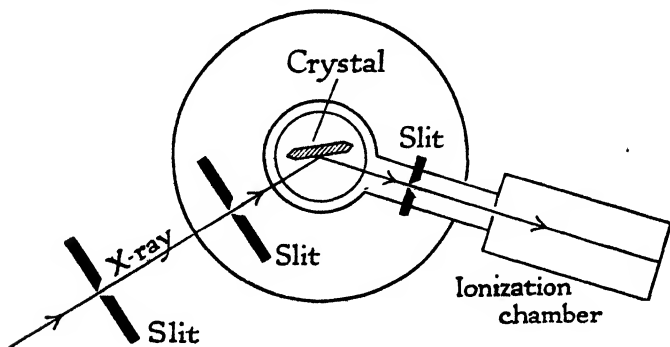
FIG. 14. THE X-RAY SPECTROMETER

of causing gaseous molecules to dissociate into oppositely-charged atoms, or ions, whose presence can be detected by an electrometer connected to plates in the ionization chamber. The whole apparatus recalls a spectrometer, in which the source of monochromatic light is the X-ray tube, while the diffraction grating is the crystal, and the place of the telescope is taken by the ionization chamber; it is in fact called an X-ray spectrometer (Fig. 14).

The application of the original methods of Laue and Bragg was limited to substances which could be obtained in crystals of reasonably large size. In a third method, independently proposed by HULL and by DEBYE and SCHERRER, this is no longer necessary, the place of the single crystal being taken by a powdery mass of small crystals, through which a beam of X-rays is passed according to the Laue method. The crystallographic axes of these small crystals, and consequently their lattice planes, are inclined at all possible angles to the incident beam, but since, for the reasons discussed in the explanation of the reflection method, the beam can only be deviated through certain specified angles, a series of concentric circles is registered on the photographic plate, and by measurement of their radii and intensities the necessary deductions

D

can be made. The discovery of the powder method has greatly increased the usefulness of X-ray analysis.

So definite and so accurate are the deductions from these methods, particularly the first two, that the wave-length of monochromatic X-rays is now usually determined by measurements on a crystalline substance whose lattice dimensions are known. On the other hand there are still many difficulties to be overcome, partly technical and partly systematic. Some crystal structures, particularly of organic substances, are so complicated that their elucidation is at present difficult, and hydrogen atoms—almost constantly present in organic compounds—are particularly difficult to place, on account of their small mass and consequent feeble power of reflecting X-rays. We shall briefly consider a few of the more interesting structures which X-ray analysis has revealed.

Crystal Structures.—All the alkali mono-halides have the sodium chloride structure except the chloride, bromide, and iodide of the heaviest member, caesium, which have what is called a 'body-centred' cubic lattice (Fig. 15) instead of the lattice already illustrated in Fig. 13. The different types of lattice found among the alkali-metal halides can be attributed to the different radii of the alkali-metal ions. Every ion tends to surround itself with as many

○ Cs
● Cl
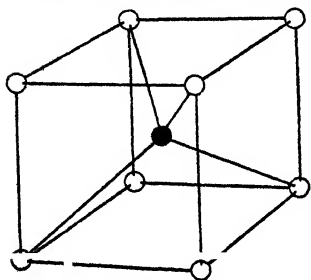
5.   THE STRUCTURE OF CAESIUM
        CHLORIDE, CsCl

ions as possible of opposite sign, and to place itself as far as possible from ions of like sign. If the ions are of like size, as in caesium chloride, the stablest structure is the body-centred cube, in which each ion is surrounded by eight others of opposite sign and eight others of the same sign. The ions of opposite sign are, however, closer to it than the others, the ratio of the distances being $\sqrt{3} : 2$ or 0·87 : 1. If one ion is much larger than the other, as in sodium chloride, this structure brings ions of like sign too close together, and is replaced by another, depicted in Fig. 13, in which each ion is surrounded by only six of unlike sign (and twelve of like sign), but in which the ratio of the distance between adjacent unlike ions to the distance between adjacent like ions is farther from unity, namely 1 : $\sqrt{2}$ or 0·71 : 1.

One of the most interesting crystals from the structural as well as other points of view is the diamond. This structure (Fig. 16) bears out in the most striking way the tetrahedral arrangement of

the valencies of carbon long since postulated by VAN'T HOFF to account for the stereochemical properties of organic compounds. It is also interesting to note how six-atom rings, which are familiar in organic chemistry, appear in the crystal structure of carbon. The well-known hardness of the diamond is no doubt to be attributed to the mechanical efficiency of this isotropic structure, and may well be contrasted with the softness of graphite, illustrated in Fig. 17. In this modification of carbon the atoms are arranged—in hexagons—in comparatively widely-spaced planes. The consequence is that graphite combines tenacity in one direction with weakness in another. The connection
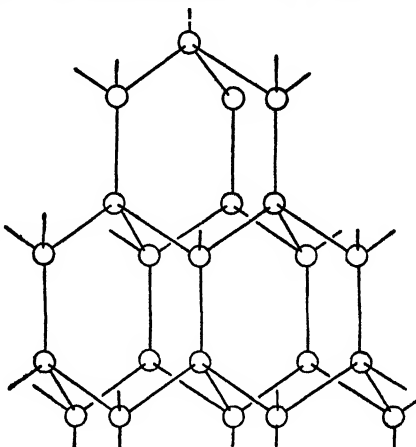
FIG. 16. THE STRUCTURE OF THE DIAMOND
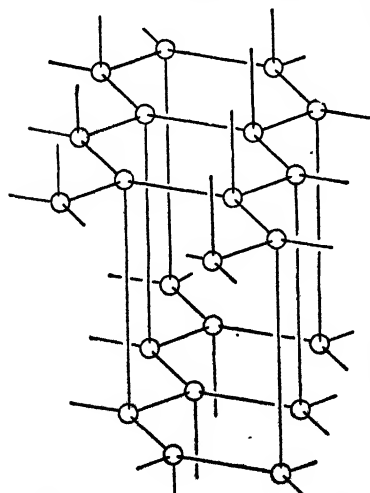
FIG. 17. THE STRUCTURE OF GRAPHITE

between the planes is so weak that they slide readily one on another, while the close arrangement within them makes them difficult to dismember. It is to these circumstances that the lubricating qualities of graphite are due.

Once more we see that the simple chemical molecule has vanished: a diamond is one immense molecule, since it is nowhere possible to find any group of atoms isolated from the rest. It is only when we come to review the structure of organic crystals that we find the identity of the molecule preserved.

The structures of diamond and graphite show that in this case at least the occurrence of allotropy can be attributed to the stability of alternative crystal arrangements. The same is true of iron, whose α, β, and δ modifications crystallize

in the body-centred cube arrangement, while the γ variety is in face-centred cubes. On the other hand, no change in structure has been detected in the transformation from the α to the β variety. This involves a change from a magnetic to a non-magnetic material, and there is other evidence to show that considerations of crystal structure will probably never be sufficient to account for all the known cases of allotropy, even among crystalline substances.

Some progress has been made in the correlation of optical activity with crystal structure. Thus the optically active properties of α- and β-quartz are probably to be ascribed to the presence of oxygen atoms arranged in spirals, which may be either right- or left-handed. The very complicated structures
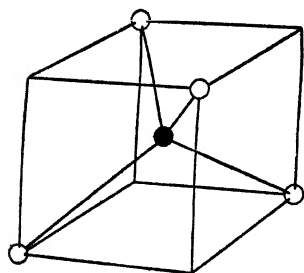
FIG. 18. THE STRUCTURE OF CALCIUM FLUORIDE, CaF$_2$

of the silicates have also been investigated; in these the predominating factor is the arrangement of the oxygen atoms, which appear to occupy a volume out of proportion to their number. The other atoms lie within the interstices of the oxygen framework.

Another type of structure is presented by fluorspar, calcium fluoride, CaF$_2$ (Fig. 18).

Peculiar interest attaches to the structure of ammonium chloride, in which the identity of the compound radical is clearly brought out (Fig. 19).

The investigation of alloys has also yielded instructive results. When the two elements forming a binary alloy crystallize in the same structure, it is usual to find that the atoms of one can be replaced step by step by the atoms of the other; this is the case when the metals form alloys in

FIG. 19. THE STRUCTURE OF AMMONIUM CHLORIDE

all proportions, and is particularly likely to occur when their atoms are of similar weight. If the elements crystallize in different structures, the structure of one is preserved until a certain critical concentration of the other is reached: the structure then changes abruptly. In mixed crystals too—a class of
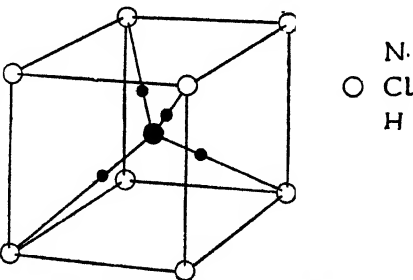
substances characterized by the possibility of variation in the proportions of the constituent compounds—similar ions can take each other's places at random in the lattice. The formation of mixed crystals is usually confined to substances of similar crystalline form. Such substances are called *isomorphous*, and it is often found that the corresponding compounds of similar elements are isomorphous, e.g. many sulphates and chromates. Isomorphism depends less, however, on valency than on the similarity of completed electron shells (Chapter XI), e.g. calcium fluoride, CaF_2, is isomorphous with sodium sulphide, Na_2S, the electron shells of the calcium and sulphide ions, on the one hand, and of the fluoride and sodium ions, on the other, being identical.

The determination of the crystal structure of organic substances is made difficult by the large number of atoms present in the crystal unit. In these substances the molecule is preserved, and it is not unusual to find that the crystal unit contains two, three, or four molecules. The molecules themselves are electrically neutral, and they probably keep their places by reason of the interaction of the unsymmetrical fields of force in the molecule. Work on benzene and naphthalene confirms the structures assigned to these compounds on chemical grounds. The structure of the fatty acids deduced from X-ray analysis fully confirms the evidence of their physical properties. These acids, whose general formula is $CH_3.(CH_2)_n.COOH$, are arranged in double layers in which the COOH groups all point inwards, while the methyl groups point outwards. Since almost the whole of the chemical activity of the molecule is concentrated in the COOH group, it is not surprising that in the crystal these groups should be found closely connected. The direction of the long chains appears not to be at right angles to the planes in which the COOH groups lie, but it is possible to calculate the length of the chain and hence to form an estimate of the extra length required for each CH_2.

While it may be doubted whether, even with its present highly developed technique of calculation, X-ray analysis will ever replace the traditional methods of organic chemistry, the situation has often arisen in which the older science can only with extreme difficulty distinguish between the few alternative structures to which it has reduced a problem. It is then that the X-ray method may prove decisive.

The Packing of Crystals.—The knowledge gained from X-ray analysis of solids has enabled us to discern the principles governing the packing of the units out of which the crystalline solid is built. If a number of equal spheres are packed into a given space as densely as possible it will be found that every sphere is symmetrically surrounded by and in contact with twelve others. This arrangement

of *close-packing* is typical of the majority of the metals, although the alkali metals show the slightly less dense packing of eight atoms symmetrically in contact with any one atom, their cubic structure resembling that of caesium chloride shown in Fig. 15, p. 88. The chief influences causing a reduction in the density of packing are (1) the crystal is composed of unlike units of different sizes, (2) the effect of ionic charges in crystals composed of ions, (3) the presence of directed valencies. Of these (1) and (2) are purely geometrical or electrostatic in origin. The comparatively open packing in diamond (Fig. 16, p. 89), in which there are only 4, tetrahedrally-disposed, nearest neighbours to any one atom, is entirely attributable to the strong tetrahedrally-directed valencies of carbon: the hardness and low compressibility of diamond being ensured in spite of the open packing, by the strength of the bonds between atoms. It has become customary to use the term ' coordination ' in describing the type of packing in terms of nearest neighbours. Thus the alkali metals show 8-co-ordination, sodium chloride and very many other ionic crystals 6-co-ordination, while diamond exhibits 4-co-ordination. The types of co-ordination occurring in crystals correspond only to the numerals 12 (close-packing), 8, 6, 4, 3, and 2. A crystal composed of unequal numbers of unlike units, such as calcium fluoride CaF_2, must contain a double co-ordination, in this case 8 : 4 co-ordination, implying that every fluorine ion F^- has 4 calcium ions Ca^{++} as its closest neighbours, but every Ca^{++} ion is immediately surrounded by 8 fluorine ions, as a careful inspection of Fig. 18, p. 90 will show. In this usage the term co-ordination has a purely geometrical meaning, which must not be confused with the chemical meaning given to this word in respect of a certain type of valency (p. 345).

Ionic Diameters.—Numerous attempts have been made to calculate the dimensions of the ions by supposing them to be rigid spheres in contact in the crystal. The results of these calculations lead to values for the ionic diameters roughly in agreement with those calculated by other methods, but to obtain closely concordant values it is necessary to restrict the comparison to salts of the same type. That differences should arise is not surprising, since there is nothing to show that the atoms or ions are rigid spheres, and what we know of the distribution of their fields of force in space does not lead us to suppose that they are either symmetrical or unyielding. It is probable that the atom has no definite size, but adapts itself to the exigencies of the structure in which it finds itself. Current estimates of atomic and ionic radii have, however, been of use in pointing the way to the probable interpretation of the X-ray data for new substances. The following are some of the values, expressed in units of 10^{-8} cm:

Li	1·52	Na	1·86	K	2·31	NH₄⁺	1·43		
Li⁺	0·78	Na⁺	0·98	K⁺	1·33	O⁻	1·40	F⁻	1·33
C	0·77	Si	1·17	N	0·73	O	0·74	F	0·72

Liquid Crystals.—Before leaving the subject of crystal structure we must refer to the so-called ' liquid crystals.' Some organic substances (e.g. para-azoxyanisole) on melting pass into a form with the fluidity of a liquid but some of the optical properties of a crystal. This peculiarity disappears when the temperature is raised above a certain limit, and a normal liquid is produced. Liquid crystals share with true crystals the phenomenon of *anisotropy*, that is to say, their physical properties (such as refractive index) depend on the direction in which they are measured. This phenomenon is never shown by true liquids. Some liquid crystals, such as ammonium oleate, when melted in small quantities on a horizontal surface, form drops whose sides are not curvilinear but arranged in small regular steps which can be made to slide one over the other.

The explanation of these curious properties is probably as follows. Substances known to form liquid crystals are presumed to have long molecules in which the chemical activity is very unevenly distributed and is chiefly concentrated at certain points. These molecules even in the liquid state tend to set themselves with their axes parallel, and it is this arrangement which simulates the appearance of crystalline form. The anisotropy of such substances as stretched rubber can also be brought out by X-ray analysis; substances in such a condition must contain a rudimentary form of crystalline structure.

GASES

Kinetic Theory of Gases.—We have shown in Chapter I how the study of gases led to Avogadro's hypothesis and the importance of this study for the determination of atomic weights. Since the time of Avogadro our ideas of the gaseous state have been extended by the development of the kinetic theory, chiefly due to CLERK MAXWELL, CLAUSIUS, BOLTZMANN and VAN DER WAALS. This theory is a corollary of the kinetic theory of heat, according to which the heat energy of a substance, whether solid, liquid, or gaseous, consists of the kinetic energy of the random motions of its particles. Absolute temperature is taken to be a measure of the average kinetic energy of the particles. The atomic and molecular theories allow these particles to be identified with molecules, for substances in a gaseous state, and the kinetic theory of

gases is based on a statistical study of the magnitude and direction of the molecular velocities.

The molecules are assumed, for purposes of calculation, to be spheres, and we must also suppose them to be perfectly elastic, since by the *Law of the Conservation of Energy* no energy can be lost in the frequent collisions between molecules. These collisions will cause the velocity and direction of a molecule to suffer frequent and violent changes, so that its rate of progress through the gas is comparatively slow, in spite of the very high velocity of molecular movements. Thus at 0° the mean speed of a hydrogen molecule is about 1·6 km. per second, but in each second it suffers about 10^{10} collisions with other molecules, so that the average distance travelled in a second, measured in a straight line, is less than 1 cm.

Distribution of Molecular Velocities.—On account of these abrupt changes of velocity the speed of any selected molecule at a given moment may have any value from zero up to a value several times the mean velocity. The distribution of the velocities is illustrated in the diagram, in which the possible values of the velocity are plotted on the horizontal axis while the vertical axis represents the number of molecules per c.c. which are moving with that velocity at a given moment. The point M
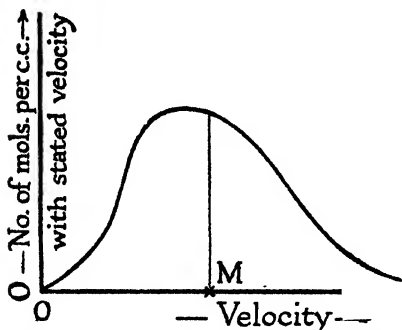
FIG. 20.   DISTRIBUTION OF VELOCITY AMONG GAS MOLECULES

marks the mean velocity, and it will be seen that molecules with a velocity in the neighbourhood of the mean are very much more numerous than molecules with very small or very great velocities. The form of the curve was worked out by Maxwell with the help of the laws of probability.

Kinetic Theory and the Gas Laws.—It can be shown that the simple laws governing the effect of temperature and pressure on the volume of a gas are in accordance with the postulates of the kinetic theory. In the calculations we shall use not the mean velocity but the root-mean-square velocity, that is, the square root of the arithmetical mean of the squares of the velocities of all the molecules at a given instant, and we shall assume that all the molecules are moving with this velocity. For a proof that this

assumption is legitimate we must refer the student to one of the larger textbooks of physics, but in passing we may point out that it does not affect the total kinetic energy of the molecules, which is a function of the sum of the squares of their velocities.

Consider a gas confined at a temperature of $T°$ Abs. and a pressure p in a cube of side a. Let the mean square velocity of the molecules at this temperature be u, and let these velocities be resolved into velocities u_x, u_y, and u_z parallel to three sides of the cube meeting in a point. Then by solid geometry $u^2 = u_x^2 + u_y^2 + u_z^2$.

Consider the component u_x along the x axis. A molecule moving parallel to the x axis with velocity u_x will strike the yz wall of the cube $\dfrac{u_x}{a}$ times per unit of time. Since it leaves the wall with an equal but opposite velocity the change of momentum at each impact is $2mu_x$, where m is the mass of the molecule, and the change of momentum per unit of time is $2mu_x \times \dfrac{u_x}{a} = \dfrac{2mu_x^2}{a}$. The change of momentum per unit of time in all directions is then $\dfrac{2m}{a}(u_x^2 + u_y^2 + u_z^2) = \dfrac{2mu^2}{a}$ per molecule, or $\dfrac{2mu^2 n}{a}$ if there are n molecules in the cube. Now these molecular impacts are the cause of the pressure exerted on the walls. The rate of change of momentum, which has the dimensions of a force, is $\dfrac{2mnu^2}{a}$ divided over the six walls of the cube, of combined area $6a^2$, or $\dfrac{mnu^2}{3a^3}$ per unit area. This force per unit area is equal to the pressure p, whence $p = \dfrac{mnu^2}{3a^3}$ But a^3 is the volume of the gas (say V), and we have agreed that the absolute temperature T is to be proportional to the kinetic energy of the particles $= \dfrac{1}{2}mnu^2$. Hence

$$\frac{pV}{T} = \text{constant or } pV = RT, \text{ where } R \text{ is a constant.}$$

The value of the constant R depends on the mass of gas which is taken: in numerical calculations it is best to remember that at 0° C. and 760 mm. pressure the molecular weight of a (perfect) gas expressed in grams occupies 22·41 litres. In heat units this brings the value of R to 1·99 calories per Centigrade degree, per gram-molecule.

This relation combines the laws usually called by the names of CHARLES and BOYLE, expressing respectively the effect of temperature and pressure on the volume of a gas. It is, however, found in

*D

practice to be only approximately correct, and for gases in the neighbourhood of their boiling-points considerable differences arise. A hypothetical gas which exactly obeys the simple gas law is called a perfect gas, and in calculations where high accuracy is not required this convention is a very useful one. Hydrogen and nitrogen approach most nearly to the behaviour of perfect or 'ideal' gases, and for this reason are used in gas thermometers.

Imperfect Gases.—The first successful attempt to give mathematical expression to the imperfections of real gases was made by van der Waals, who pointed out two sources of inaccuracy in the simple form of the calculation:

1. The volume V must be reduced by an amount b to allow for the space occupied by the molecules, which according to the theory is $\dfrac{b}{4}$.

2. In the interior of the gas the attractive forces between the molecules operate in all directions and therefore cancel out, but at the surface of the containing vessel, or at the manometer, where the pressure is actually measured, the attractive force of the molecules operates inwards and is unbalanced from the outside. This drag manifests itself as a reduction in the pressure, and is proportional both to the number of molecules on the surface of the gas on which the attraction is working and to the number of molecules behind them to which the force is due. Both these are proportional to the density of the gas, which, for a given mass of gas, is inversely proportional to the volume, so a term inversely proportional to the square of the volume, say $\dfrac{a}{V^2}$ where a is a constant, must be added to the pressure in the simple gas equation.

The equation therefore becomes:

$$\left(p+\frac{a}{V^2}\right)\left(V-b\right)=RT,$$

where a and b are constants specific for each gas, calculated from the observed variation of pV with pressure and temperature.

Expanded, this becomes:

$$pV-pb+\frac{a}{V}=RT,$$

neglecting the small product of the corrections. Since both a and b are positive, the variations from constancy of pV may take either a positive or negative direction, according to the conditions. The nature of these variations does indeed vary from gas to gas. The diagram (Fig. 21) shows pV plotted against p in atmospheres

from AMAGAT's results. Whereas hydrogen at 0° C. shows a continual increase in pV with pressure, nitrogen at 0° C. shows a slight minimum, and ethylene at 100° C. a pronounced minimum. Other gases, such as carbon dioxide, with comparatively high boiling-points, resemble ethylene in their behaviour.
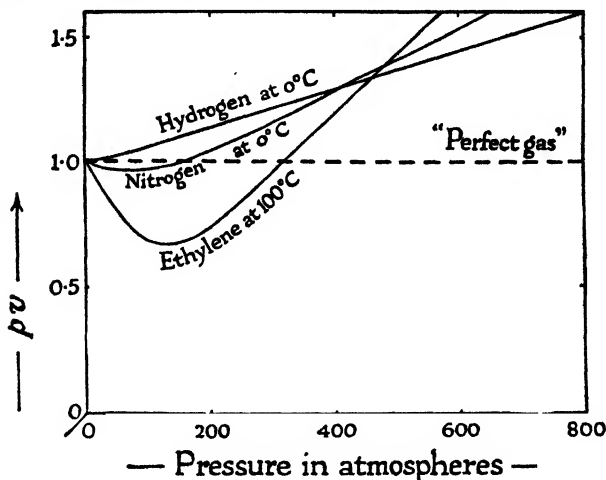
FIG. 21. VARIATIONS FROM BOYLE'S LAW

Liquefaction of Gases.—These deviations from the basic laws of ideal gases have important practical applications to the liquefaction of gases and the working of refrigerators. Since pV is approximately equal to RT, and T is proportional to the kinetic energy of the molecules, any change in pV must involve a change in the kinetic energy of the molecules. If such a change in pV takes place on free expansion of the gas, the excess or deficit in kinetic energy must be derived from a spontaneous change in the temperature of the gas. That this does actually happen was shown by the celebrated JOULE-THOMSON 'porous plug' experiment. A gas was allowed to flow slowly through a porous partition from a region of high pressure to a region of low pressure and the small change in temperature was observed. In this and other experiments it was found that most gases (hydrogen was an exception) showed cooling under these conditions, whereas hydrogen grew slightly warmer. Since the experiments were made at not very high pressures, the results confirm those shown in the diagram. For most gases at moderate pressures, pV decreases with increasing pressure and therefore increases on expansion: the energy required for the

increase must come from the thermal energy of the gas, whose temperature therefore falls.   At lower temperatures the exceptional behaviour of hydrogen disappears, and it suffers cooling like other gases.

The cooling of gases on free expansion is put to use in liquefaction plants.   The gas is first compressed in a pump to some 200 atmospheres, and is then passed through a cooling coil where the heat produced in compression is absorbed.   From the cooler the gas passes to a well-insulated coil surrounded by the return current of cold gas. The object of this coil, which is usually very long, is to bring the gas inside and out to nearly the same temperature.   It is therefore made of copper and is often double, the entering gas being inside and the issuing gas outside.   At the bottom of the coil is the jet at which free expansion takes place, and after the plant has been running for some time drops of liquid collect in the receiver.

FIG. 22.   LIQUEFACTION OF GASES (DIAGRAMMATIC)
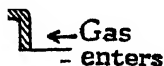
A modification of the process is necessary if hydrogen is to be liquefied, since at room temperature hydrogen is not cooled by free expansion, but, on the contrary, slightly warmed.   Below −80° cooling takes place, and hydrogen is therefore cooled to well below this temperature with liquid air before it is admitted to the expansion plant.

Diffusion.—GRAHAM's *Law of Diffusion* is an interesting confirmation of the kinetic theory of gases which in recent years has been put to use in the separation of isotopes (p. 319).   Graham found that the rate at which gases at equal temperatures and pressures diffused through small orifices was inversely proportional to the square root of their densities.   We know from Avogadro's hypothesis that under these conditions the density is proportional to the molecular weight, so that molecular weights can be written instead of densities in Graham's law.   Thus oxygen, with nearly sixteen times the molecular weight of hydrogen, diffuses only one-quarter as fast.   The explanation is as follows.   The mean square

velocity is connected with the absolute temperature by the relation $\dfrac{mnu^2}{3}=pV=RT$ already deduced. The mean square velocity is therefore inversely proportional to the square root of the molecular weight. Now the rate of diffusion depends on the number of molecules which strike one of the small orifices (e.g. the pores of meerschaum) in unit time, and this must be proportional to the velocity, or inversely proportional to the square root of the molecular weight.

Dalton's Law of Partial Pressures.—In such experiments as these the gases may be in the same vessel at the same time without disturbing the relationships, provided that their partial pressures are considered, and not the total gas pressure. The partial pressure of the gas is the pressure which it would exert if it alone filled the space in which the mixture is confined. The total pressure is the sum of the partial pressures (DALTON'S *Law*), and this obviously follows from the kinetic theory, but experiment sometimes reveals differences when the gases under consideration are those whose behaviour under changes of temperature and pressure shows much deviation from the gas laws.
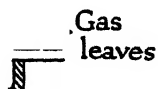
FIG. 23. KATHAROMETER

Thermal Conductivity.—The thermal conductivities of gases depend on the average distance travelled by the molecule between collisions (called the 'mean free path'), the complexity of the molecule, and the molecular weight. Since this property can be rapidly measured in an apparatus designed for the purpose, and since it varies very greatly for different gases (e.g. hydrogen has more than ten times the conductivity of carbon dioxide), instruments called *katharometers* working on this principle are sometimes used for the analysis of gas-mixtures in factories, in preference to the more accurate but far more laborious methods of chemical analysis. A coil of thin platinum wire forming one arm of a Wheatstone's bridge is kept, by the current flowing through it from the bridge,

at a temperature some five or ten degrees above that of its surroundings. The gas stream, first cooled to the temperature of the apparatus, is made to flow past the wire at a fixed rate. The resistance of the wire depends on its temperature, which in turn depends on the cooling effect of the gas, so alterations in the thermal conductivity of the gas are immediately reflected in the bridge readings. The apparatus is peculiarly well adapted to furnace control by analysis of the flue gases.

Molecular Heats.—The molecular heats of gases, though difficult to measure with accuracy, are of great theoretical importance. Two molecular heats must be distinguished, at constant volume and at constant pressure, denoted by C_v and C_p. The molecular heat at constant volume is the number of calories required to raise the temperature of one gram-molecule of the gas through one Centigrade degree, the volume being kept constant. Under these conditions the pressure rises, and to reduce the pressure to the original value the gas must be allowed to expand. This implies the performance of work, and it is easily seen from the equation $pV = RT$ that the extra heat required, to offset this work, is R calories=roughly 2 calories $= C_p - C_v$. Now $pV = \dfrac{mnu^2}{3}$, and the total kinetic energy of translation of the molecules, which we may call E, is $\dfrac{1}{2}mnu^2$.

$\therefore pV = \dfrac{2}{3}E$ and $E = \dfrac{3}{2}RT$. For unit increase in T the increase in E is therefore equal to $\dfrac{3}{2}R$=nearly 3 calories. If the only kinetic energy possessed by the gas molecules were their translational energy, this would be equal to C_v, and this is indeed found to be true for all the monoatomic gases so far investigated—mercury vapour and the inert gases. But when a polyatomic gas molecule is heated, not all the energy supplied goes to increase the kinetic energy of the motion of the molecule through the gas. Some energy is required to increase the rotational energy of the molecule and also the energy of relative motion, probably oscillations, of the atoms within the molecule. These two together may be called the internal energy. Then

C_v=translational energy+internal energy (if any)   and

C_p=   ,,   ,,   +   ,,   ,,   ,,   +external work

or $\dfrac{C_p}{C_v} = \dfrac{3+\text{internal energy}+2}{3+\text{internal energy}} = \dfrac{5+\text{internal energy}}{3+\text{internal energy}}$.

Monoatomic gases have no internal energy, and consequently

$\dfrac{C_p}{C_v} = \dfrac{5}{3} = 1.67$. This is in accordance with experiments on the velocity of sound in these gases, from which the ratio of the molecular heats can be calculated. The more complex the molecule, the greater the internal energy and the nearer to unity the value of $\dfrac{C_p}{C_v}$. This again is in accordance with experiment, as the following table shows:

Gas:	Argon	Hydrogen	Carbon dioxide	Benzene	Turpentine
$\dfrac{C_p}{C_v}$:	1.65	1.41	1.30	1.09	1.03

Viscosity.—On the basis of the kinetic theory equations have been developed connecting the viscosity [1] of gases with the molecular weight and the mean free path. The viscosity can be determined experimentally, and if the molecular weight is known the molecular diameter can be calculated. The results of these calculations are in indifferent agreement with the values deduced directly from measurements on crystals with X-rays, the difference being usually about 40 per cent. The same applies to calculations based on the value of the constant b in van der Waals's equation; it will be remembered that this is supposed to be proportional to the space occupied by the molecules in the gas. These and other results make it probable that the molecular diameter is not a fixed magnitude, independent of conditions.

LIQUIDS

Pure Liquids.—While the recently introduced X-ray methods of crystal analysis have thrown much light on the nature of the solid state, and while the kinetic theory has done the same for gases, our knowledge of pure liquids (as distinct from solutions) is still rudimentary. That the molecules in the interior of a liquid are in motion is shown by the fact that two mutually soluble liquids placed in contact diffuse into each other until the system is homogeneous. The kinetic theory accounts for the difference between the liquid and gaseous states by assuming that in the former the molecules have been brought so close together that the intermolecular attraction is sufficient to overcome the tendency of molecules to leave the system. Surface tension is caused by the inward pull of the body of the liquid on the surface molecules.

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[1] The viscosity of a liquid or a gas is the force per unit area between two parallel planes unit distance apart when the liquid or gas flows between them and parallel to them with unit difference of velocity at the two planes.

Only molecules with exceptionally high velocities are able to overcome this attraction and break through the surface, and the vapour pressure at any temperature is a measure of the number of molecules for which this is possible. As the temperature is raised the concentration of molecules in the vapour phase approaches the concentration in the liquid phase; when these two concentrations become equal the surface tension is reduced to zero, the liquid-vapour surface disappears, and the *critical temperature* is reached.

While there is little doubt that this kinetic view of evaporation is correct, not much else is certain. Ignorant as we are of the law of force between molecules in close contact we cannot calculate the mean free path or the volume of the molecules. Even the determination of the molecular weight of pure liquids is a problem of much difficulty. In this section we shall confine ourselves to a short discussion of this problem and to an account of some recent experiments which tend to show that certain types of molecules at least are at the surface arranged in a regular fashion.

Molecular Weight and Association.—There is no reliable method of determining the molecular weight of a pure liquid. Much evidence has been accumulated that a large class of liquids is associated, that is, the apparent molecular weight is greater than that attributable to molecules in the vapour at temperatures well above the boiling-point.

The molecular weight of a liquid may very well be more, but can hardly be less, than the molecular weight of its vapour. Thus if vapour-density measurements betray the presence of multiple molecules in the vapour, as in the vapour of acetic acid, hydrogen fluoride, or, to a much less degree, water, there is a strong probability that these liquids are associated. The molecular weight of a liquid when dissolved in another can be accurately measured by the methods outlined in Chapter IV, and a high result in such experiments is evidence of association in the pure liquid, though quantitative deductions from such data are unjustifiable. Water, for instance, when dissolved in other liquids, has a molecular weight varying according to the solvent and concentration up to nearly double the value corresponding with the simple formula H_2O.

An abnormally high value for the latent heat of vaporization points in the same direction. On vaporization associated liquids usually suffer a reduction in the mean molecular weight, and this breakdown into smaller units absorbs heat which must form part of the experimentally determined latent heat. Liquids which are in fairly close agreement with the relation called TROUTON's *Rule*:

$$\frac{M.l}{T} = \text{constant (about 21 cal. per °C.)},$$

where M is the molecular weight, l the latent heat of vaporization, and T the absolute temperature of the boiling-point, are regarded as non-associated. Liquids which show considerable departure from this rule (which, though introduced as an empirical relation, is a simplified form of an equation with a thermodynamic basis) are believed to be associated. Association is also indicated by an abnormally high viscosity. The best criterion of this effect is the ratio of the viscosity to the *molecular volume* (the formula weight divided by the density).

Associated liquids show values of this ratio very much in excess of those found for normal liquids.

Association in liquids can now be viewed from a new angle as the result of X-ray analysis. The oxygen atoms in ice are in tetrahedral 4-co-ordination very similar to that of carbon atoms in diamond. The openness of this packing arrangement is emphasized by a simple calculation.
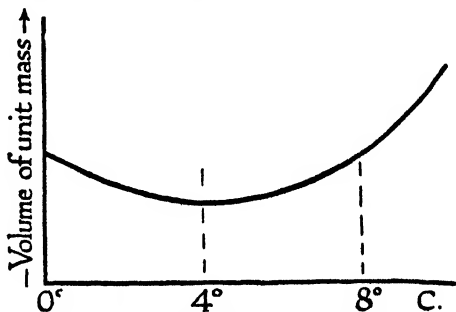
FIG. 24. EXPANSION OF WATER

From our fairly exact knowledge of the dimensions and weight of the steam molecule H_2O we can easily find that were an assemblage of these molecules close-packed in 1 c.c., the weight would be nearly 2 gm., while the actual specific gravity of ice is 0·916. As in diamond, the open structure is conditioned by directed valencies, exercised in a manner not yet fully understood, through the hydrogen atoms, one of which lies between each pair of oxygen atoms, and probably in the line of their centres. Such so-called 'hydrogen bonds' appear to be not uncommon, cases being known in which not only pairs of oxygen atoms but two fluorine atoms, or nitrogen and fluorine (as in ammonium fluoride), or nitrogen and oxygen appear to be held together by such bonds. When ice is melted the quite regular and complete bonding operating throughout the ice crystal is broken here and there, and a slightly denser packing, corresponding to an increase of about 10 per cent in density, is achieved. As the above calculation showed, if all or nearly all the oxygen-oxygen links were broken the increase of density would be over 100 per cent. As the liquid water is heated there is probably a slight but progressive further rupture of the bonds, but the high latent heat at the boiling-point indicates that even at this temperature volatilization is far from a purely physical process. Above 4° C. the thermal expansion conceals the effect of

the closer packing. It is clear that this picture does not permit us to assume the water contains definite polymers $(H_2O)_n$. We should better regard water as essentially ice, in which a small proportion of the bonds are continually fractured and repaired at random points. We may legitimately expect a similar constitution in the alcohols and other liquids recognized as 'abnormal.' The conception of molecular weight is clearly meaningless when applied to ice, since throughout the crystal the bonding is uniform, and co-extensive with the crystal. On the view put forward above the conception is also without meaning for liquid water. If as now seems probable all liquids show structure in some degree, then we must modify the earlier attitude of regarding liquids as highly compressed gases based on the van der Waals conception of the continuity of the liquid and gaseous states. Such a view is probably correct only in the neighbourhood of the critical point.

The Parachor.—Numerous methods of estimating the molecular weight are based on arbitrary formulae involving the surface tension, a property which is undoubtedly closely connected with the occurrence of association. These methods have not been uniformly successful, but in recent years there has become available a method which allows us to decide with some approach to certainty whether a liquid is associated or not. In 1924 it was shown (1) that for a non-associated liquid the value of the expression $\frac{M}{D-d} \cdot \gamma^{\frac{1}{4}}$ was a constant independent of the temperature (M is the molecular weight, D the density of the liquid, d that of the vapour, and γ the surface tension); (2) that this constant was an additive function of fixed values which can be assigned to each atom. Extra values must also be allowed for some special types of combination, such as double bonds or rings.

This constant is called the *parachor*. It has been applied in both organic and inorganic chemistry in attacking questions of structure. Associated liquids show wide variations from the calculated values, but as with Trouton's rule, quantitative deductions cannot be drawn from these variations.

The liquids which by these tests are found to be associated include water, hydrogen peroxide, the alcohols, the fatty acids, the acid amides, hydrogen fluoride, and liquid ammonia. It is significant that all these liquids contain hydrogen, and in them 'hydrogen bonds' may well be operative, as mentioned above.

Characteristics of Associated Liquids.—Meanwhile we may mention certain other characteristics of associated liquids which, while scarcely definite enough to serve as conclusive evidence of association, are of significance when the group is considered as a whole.

1. Associated liquids are usually miscible in any proportion

with each other, but only in limited proportions with normal liquids, while normal liquids are miscible with each other, but not with associated liquids.

2. The physical properties of mixtures of associated liquids seldom vary in a linear manner between those of the constituents, whereas with normal liquids a nearly linear relation is usual. The reason for this is the effect which associated liquids have on each other's molecular constitution: the structures present in the pure liquids are to some extent broken down and new structures formed. The diagrams show the viscosities of typical pairs of associated and normal liquids:

Associated : Water and Methyl alcohol

Normal : Benzene and Carbon tetrachloride
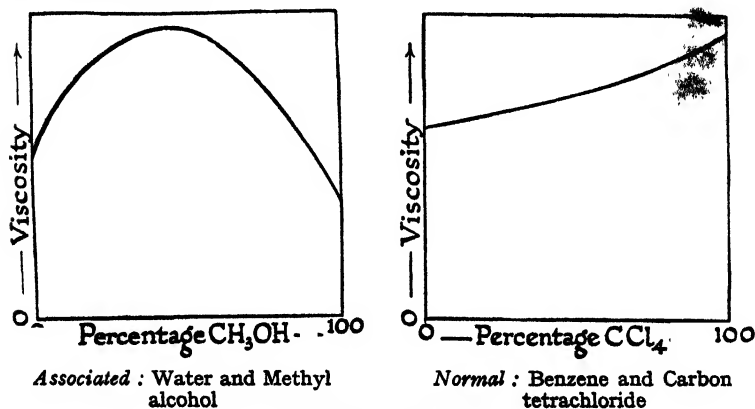
FIG. 25. VISCOSITY OF MIXED LIQUIDS

3. Associated liquids have high dielectric constants.[1] The values for a few typical liquids of either class are:

Associated			*Normal*		
Water	.	. 82	Carbon tetrachloride	.	2
Formic acid	.	. 58	Acetic anhydride .	.	21
Methyl alcohol	.	. 33	Benzene	.	2
Acetamide .	.	. 59	Ether . . .	.	4

Exceptions are, however, found, e.g.:

Acetic acid .	. .	. 6	Nitrobenzene	.	. 36

4. Associated liquids have the power of dissociating suitable solutes into ions (Chapter IV). There is no doubt that this is

[1] The dielectric constant or specific inductive capacity of a substance is the ratio between the capacity of a condenser when that substance is used as dielectric and the capacity when air is used as dielectric.

partly due to their high dielectric constant, which facilitates the separation of the ionic charges; but the residual affinity of the solvent molecules probably has some effect, since the forces which cause the molecules of the pure solvent to combine may be equally effective in combining them with the ions of the solute, thereby promoting the dissociation of the latter. Thus slightly basic solvents promote the ionization of acids, and vice versa.

The correct expression for the ionization of such a body as acetic acid in aqueous solution is not $CH_3CO_2H \rightleftharpoons CH_3CO_2' + H'$, but $CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2' + H_3O'$.

5. Associated liquids have abnormally high boiling-points. Since volatility is nearly always reduced by increase in the molecular complexity there is nothing surprising in this. The question whether the boiling-point is abnormally high or not must be decided by comparison with similar compounds. The comparison of the boiling-point of water with that of similar substances is instructive. The thioethers, in which the oxygen atom of the ether has been replaced by sulphur, boil about 59° above the corresponding ether. Since hydrogen sulphide boils at −61° it is reasonable to suppose that water, if normal, should boil at −61°−59°= −120° or thereabouts; the true boiling-point is no less than 220° higher, and the difference is ascribed to association.

Films of Polar Molecules.—This name has been applied to molecules in which nearly all the chemical activity is concentrated at one end. The best-known examples of this class are the fatty acids, which have the formula $CH_3.(CH_2)_n.COOH$. While the lowest members of the series are liquid at the ordinary temperature the melting-point rises with molecular weight, and such a compound as palmitic acid, $CH_3.(CH_2)_{14}.COOH$, melts at 63°. The higher members are practically insoluble in water, and a single drop of the molten acid placed on a water surface spreads out into a thin film. If the volume of the drop (or its weight and density) is known, the thickness of the film can be calculated from measurement of its area; and this thickness is found to be little more than the length of a single molecule of the fatty acid, as calculated from X-ray measurements. It is also interesting to compare this result with measurements on the thickness of soap-films. The black or thinnest part of these films, which appears just before they burst (unless this is prevented by checking evaporation), is found to be just two molecules thick: there can be little doubt that in these films the COOH groups of the two molecules face inwards and are in contact, while the CH_3 groups face outwards to the air. This suggests that in the films formed on water the COOH groups are all on the water surface and the CH_3 groups all on the top of the film, and this has been proved by ADAM and

others, using a modification of the original oil-spreading method of LORD RAYLEIGH.

A shallow trough of distilled water is fitted with a movable strip suspended on the surface of the water by a rigid wire framework not shown in the diagram (which is a plan). By attaching weights to the upper part of this framework a known force can be applied to the strip in a direction causing it to move from right to left.

The water surface is first freed from floating impurities by drawing the edge of a piece of paper over it: a drop of a benzene solution containing a known weight of the fatty acid is then placed on the water in the left-hand part of the trough. The benzene evaporates, and the resulting film is compressed into the left-hand end of the trough by moving the strip. During this process the film tends to escape round the ends of the strip; this must be prevented by jets of air, as shown in the diagram. A point is
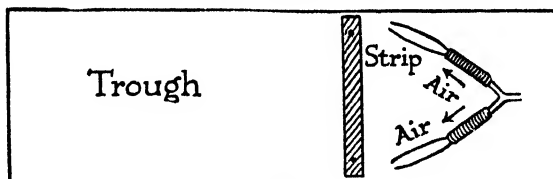
Plan
FIG. 26. FATTY ACID FILMS ON WATER

then reached at which the film, which has hitherto required scarcely any force to drive it into the left-hand end of the trough, suddenly begins to display rigidity. The film has now attained an area beyond which it cannot be compressed without collapse. This area was found to be the same per molecule for all the fatty acids examined, and clearly corresponds with the area which the COOH group occupies on the surface of the water when the molecules are in contact with their axes parallel. The area is also in good agreement with X-ray crystal measurements on the fatty acids. If the force is increased beyond that needed to keep the molecules in contact, the film crumples and in parts becomes more than one molecule thick.

The question whether the fatty acid in the film is in the liquid or the solid state is a matter merely of definition. If these films are gradually heated, a temperature is reached at which a change takes place analogous to a change of state: the minimum area of the film before crumpling suddenly increases. If the temperature is increased still further the film continues to expand slowly, and it is interesting to note that the coefficient of expansion is now the same as that of a gas. At these temperatures the mutual

attraction of the molecules is not sufficient to overcome the force of thermal agitation, which presumably takes place in two dimensions only.

SUGGESTED FOR FURTHER READING

BRAGG, W. H. and W. L.: *The Crystalline State.*
EVANS: *Crystal Chemistry.*
KNUDSEN: *The Kinetic Theory of Gases.*
ADAM: *The Physics and Chemistry of Surfaces* (1941).
WELLS: *Structural Inorganic Chemistry* (1950).

CHAPTER III

DYNAMICS OF CHEMICAL CHANGE

Effect of conditions on chemical change—Le Chatelier's Law—Reversible reactions—The decomposition of hydrogen iodide—Reaction velocity—The Law of Mass-Action—Heterogeneous systems—Kinetic order of reaction—Unimolecular reactions—Pseudo-unimolecular reactions—Velocity equation for a unimolecular reaction—Bimolecular reactions—Rapid consecutive reactions—Effect of pressure—Concentration of the reactants—Inhibition of reactions—Reactions in the human body.

Appendix—Observations on a unimolecular reaction.

Effect of Conditions on Chemical Change.—All chemical reactions, with the exception of the radioactive changes which will be dealt with later (Chapter X), are influenced by the conditions under which they take place. In this chapter we shall begin the discussion by referring to the effects of temperature, pressure, and the concentrations of the reacting substances, and we shall subsequently have to deal with the influence of light, various kinds of electric current or discharge, the presence or rigid exclusion of catalysts, and the nature of any surfaces in the reaction mixture, as well as with the energy relations that determine the course of the reaction.

In investigating a reaction we are concerned with the *nature* of the products, the *relative quantities* of each present when the reaction is finished, the *velocity* with which they are formed, and the *liberation* or *absorption of heat*. All these may be, and usually are, affected by variation in the conditions specified in the previous paragraph, which must therefore be carefully controlled when measurements of any kind are to be made. We cannot begin better than with Le Chatelier's *Law*, a principle of absolutely general application that often supplies the key to the behaviour of a system.

Le Chatelier's Law.—' If any change in the conditions of a system in equilibrium causes the equilibrium to be displaced the displacement will be in such a direction as to oppose the effect of the change.'

The applications to changes of temperature and pressure are important and obvious. Consider the solubility of a substance such as potassium chloride which dissolves in water with absorption of heat. In a saturated solution the solid is in equilibrium with

the solution, that is, in any interval of time as much of the salt dissolves as is precipitated. If now heat be supplied to the system the principle tells us that it will behave in such a way as to absorb it, that is, more potassium chloride will dissolve. This shows that the solubility of potassium chloride increases with the temperature, and the same reasoning can be applied to all substances which absorb heat when they dissolve. From an observed increase in the solubility with temperature we can also deduce an absorption of heat on solution, and vice versa, and in the same way it can be shown that heat must be absorbed in the fusion or evaporation of any substance. The application to changes of pressure is equally simple. Consider a mixture of ice and water at 0° under atmospheric pressure. If now the pressure be increased the system will change in such a way as to yield before the increased pressure by a reduction in volume, that is, the ice will melt, and to freeze it again under the new pressure it will be necessary to lower the temperature. Otherwise expressed, the melting-point of ice is reduced by increasing pressure because a given weight of ice at 0° occupies a greater volume than an equal weight of water at the same temperature. The reverse is true of most other substances, whose melting-points thus rise with increasing pressure.

Reversible Reactions.—The final result of many of the reactions with which we are acquainted appears to be unaffected by variation in the conditions in which they are carried out. They proceed more or less quickly to a definite end at which the whole of the reactants, except any which may have been in excess, have been consumed, and only the products remain. Such actions are called *irreversible.* Thus if a current of nitric oxide at room temperature is allowed to escape into the air, the whole of the gas combines with atmospheric oxygen to form nitrogen ' peroxide.'

$$2NO + O_2 \rightarrow N_2O_4.$$
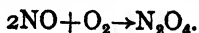
Careful analysis will show that the resulting mixture contains no detectable quantity of the lower oxide. On the other hand, reactions are known which when once started proceed with a gradually decreasing velocity and finally appear to come to an end, not when the whole of the reactants have been decomposed, but at an intermediate stage at which some of the reactants are still present together with the products. If now in another experiment the pure products in equal quantity are allowed to react, the change will proceed backwards until the same intermediate stage is reached. The reaction is in fact *reversible.* Under given conditions of temperature and pressure, the final stage will be the same whether we start with the original reactants or with the products in quantity equivalent to them. At this stage no reaction in either direction can

be detected and the system is in equilibrium, but it is more natural to suppose that both reactions are proceeding with equal and opposite velocities, that is, that the system is in *dynamic* rather than static equilibrium. The velocity of the change in either direction under given conditions can usually be calculated, and the advantage of the idea of dynamic equilibrium is that it shows the connection between reaction velocity and the stage at which equilibrium is reached.

Closer examination of many apparently irreversible reactions will show that they only appear to be so because under the chosen conditions the equilibrium lies so far on one side as to be indistinguishable from completion of the reaction. To take the case quoted above, we have only to heat nitrogen peroxide to, say, 700° for the back reaction to take place, and at about 1200° the decomposition of the peroxide into nitric oxide and oxygen appears itself to be complete and irreversible. At intermediate temperatures perceptible quantities of both reactants and products are present at equilibrium. When we say, therefore, that a reaction is irreversible we mean nothing more than that under the chosen conditions the reactants are at equilibrium present in such small concentration as to escape detection.

The Decomposition of Hydrogen Iodide.—As an example of a reversible reaction consider the dissociation of gaseous hydrogen iodide into hydrogen and iodine:

$$2HI \rightleftharpoons H_2 + I_2.$$

If heated to e.g. 350° in a constant-temperature air-bath, hydrogen iodide will decompose in agreement with the equation and with gradually decreasing velocity, but when the reaction appears to have come to an end there will still be found hydrogen iodide in the bulb, in addition to hydrogen and gaseous iodine. If equimolecular quantities of hydrogen and iodine in total weight equal to that of the hydrogen iodide taken in the first experiment be now heated to this temperature, they will combine with gradually decreasing velocity until an equilibrium state is reached which will be absolutely identical with the first. This reversibility of the reaction is expressed by the arrows of the equation. If a mixture of hydrogen, iodine, and hydrogen iodide in the proportions of the equilibrium mixture be heated to 350° no change in composition will take place, but if any other mixture containing equimolecular quantities of hydrogen and iodine, together with hydrogen iodide, be heated to this temperature, a reaction will take place until the equilibrium proportion is reached.

Reaction Velocity.—We now have to consider the velocity with which the forward and back reactions proceed. Before a hydrogen

molecule can combine with an iodine molecule it must come in contact with it by collision. The probability that in a short interval of time a given hydrogen molecule will collide with an iodine molecule will obviously be proportional to the number of iodine molecules in its neighbourhood, that is, to the number of iodine molecules per cubic centimetre, and will in fact be proportional to the concentration of iodine. Of a thousand hydrogen molecules the number which will combine per second is therefore proportional to the iodine concentration. The total number of molecular combinations that take place per second is therefore also proportional to the number of hydrogen molecules per cubic centimetre, that is, to the concentration of the hydrogen. If the total amount of hydrogen and iodine present at a given moment is a and b gram-molecules respectively, and the volume of the reaction vessel is V cubic centimetres, the velocity of combination, which represents the rate at which hydrogen iodide is formed, is

$$\bullet \; k_1 . \frac{a}{V} . \frac{b}{V} = k_1 . \frac{ab}{V^2}.$$

where k_1 is a constant. Now let $\frac{c}{V}$ be the concentration of hydrogen iodide at any moment in gram-molecules per cubic centimetre. Then the velocity with which the hydrogen iodide will decompose is proportional to the number of collisions per second between two hydrogen iodide molecules, which is, as before,

$$k_2 . \frac{c}{V} . \frac{c}{V} = k_2 . \frac{c^2}{V^2},$$

where k_2 is a constant. When the reaction has reached equilibrium the rate at which hydrogen iodide is formed must be equal to the rate at which it decomposes; hence, at equilibrium:

$$k_1 . \frac{a_e b_e}{V^2} = k_2 . \frac{c_e^2}{V^2},$$

or $\dfrac{\dfrac{a_e}{V} . \dfrac{b_e}{V}}{\left(\dfrac{c_e}{V}\right)^2} = \dfrac{k_2}{k_1} = K$, where K is a constant called the *equilibrium*

constant. The suffix $_e$ denotes the amount present at equilibrium. Equations of this kind are often written in the form:

$$\frac{[H_2] \, [I_2]}{[HI]^2} = K,$$

where the square brackets indicate concentration, or, in the case of gases, pressure.

It will be noticed that the expression for the equilibrium constant K has been brought into harmony with the chemical equation

$$2HI \rightleftharpoons H_2 + I_2 \qquad (a)$$
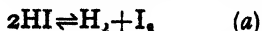
by the assumption that hydrogen iodide decomposes and hydrogen reacts with iodine only as the result of collisions between pairs of molecules. That such is the mode of action in the dissociation and formation of hydrogen halides is by no means immediately obvious, for we could imagine at least one alternative mode, such as (1) $HX \rightleftharpoons H + X$; (2) $H + HX \rightleftharpoons H_2 + X$; (3) $2X \rightleftharpoons X_2$, where X represents the halogen. The final effect of this succession of changes is of course identical with that of the single equation (a), and it can easily be shown that the alternative scheme will not affect the expression for K. For the three equilibria (1), (2), and (3) we may write:

$$[H][X]/[HX] = K_1, \quad [H_2][X]/[H][HX] = K_2, \quad [X_2]/[X]^2 = K_3,$$

and we see that $\quad K_1 K_2 K_3 = [H_2][X_2]/HX]^2 = K.$

Nevertheless the modes of reaction differ radically when considered as chemical processes, and only experimental study can decide between them. It may be mentioned that (a) is found to be a true representation for hydrogen, iodine, and hydrogen iodide, but for hydrogen, bromine, and hydrogen bromide there is evidence that the mode of reaction is by way of such a succession of changes as (1), (2), and (3).

The Law of Mass-Action.—The relation that we have above deduced is a special case of what is called the *Law of Mass-Action.* GULDBERG and WAAGE in 1864–7 developed by experimental studies the principle that *the rate at which a substance reacts is proportional to its active mass,* by which is to be understood its molecular concentration. The kernel of the theory is the idea of dynamic equilibrium, which is indeed rather more than a convenient figment. For if hydrogen and iodine molecules—or a fixed proportion of them—combine when they collide, there is no reason to suppose that they will suddenly cease to do so when an equilibrium concentration of hydrogen iodide has been formed, nor is it probable that the decomposition of hydrogen iodide molecules is arrested by the presence of a certain concentration of hydrogen and iodine.

The considerations of the preceding paragraph encourage us to assume that the law of equilibrium will not depend on the actual chemical processes by which equilibrium is attained, and to generalize our results. If n molecules of A react with m molecules of B, etc., in accordance with the equation

$$nA + mB + pC + \ldots \rightleftharpoons uL + wM + xN + \ldots$$

at equilibrium the expression

$$\frac{[A_e]^n [B_e]^m [C_e]^p}{[L_e]^u [M_e]^w [N_e]^z}$$ (or its reciprocal)

will be a constant. Though the derivation was from a gas reaction, the law can equally well be applied to reactions that take place in solution. Nor is it confined to homogeneous reactions, by which is meant reactions which take place entirely in one phase, though a little further explanation is required before it can be applied to heterogeneous systems. Fortunately this law of mass action does not ultimately rest on our not wholly convincing argument based upon reaction velocities. It can be derived in the above form independently by the methods of thermodynamics, of which science the characteristic feature is that the results of its applications are independent of mechanism, provided this satisfies certain general requirements, such as perfect reversibility. An alternative description of the law of mass-action is the law of mobile equilibrium. This phrase emphasizes a fundamental feature of the law, for one or more of the concentrations in the numerator or denominator of the expression for K may be arbitrarily changed; then, provided the temperature is unchanged, the remaining concentrations will adjust themselves till the original value of K is restored. K itself can only be changed by a change of temperature.

Heterogeneous Systems.—Consider the decomposition of calcium carbonate into quicklime and carbon dioxide:

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

The reaction is reversible, but how can we speak of the concentration in the gas phase of a non-volatile substance such as calcium oxide? There is, in fact, no need to measure it, even if it could be measured, and it is necessary merely to note that it represents the vapour pressure of the oxide at the given temperature. Every substance, however far below its boiling-point, has some vapour pressure, and this pressure is independent of the weight of substance present, so long as some remains at equilibrium. The active mass of solids in the gaseous phase under given conditions of temperature and pressure is therefore a constant, and such an equation as

$$\frac{[CaO] [CO_2]}{[CaCO_3]} = constant \ (K_1) \text{ becomes } [CO_2] = constant \ (K_2).$$

a conclusion which can readily be verified by experiment. If calcium carbonate be heated to a constant temperature in a closed evacuated vessel, it will decompose until the pressure of carbon dioxide reaches a fixed value depending on the temperature but

independent of the size of the vessel or the weight of calcium carbonate, provided that there is enough of the solid originally present for some to remain undecomposed at equilibrium. If the carbon dioxide is pumped away or allowed to escape from the vessel, the carbonate will continue to decompose till none remains; if, however, carbon dioxide at higher pressure is forced into the vessel, some of the gas will combine with the calcium oxide until the pressure has been restored to its equilibrium value.

The constancy of the active mass of a solid in the gas phase can be extended to the liquid phase, and is in fact only another way of stating the well-known phenomenon of *saturation*. If, for example, sugar and water are shaken up together at a fixed temperature, and there is not enough water to dissolve all the sugar, a point will be reached when no more sugar will dissolve. The solution is now saturated with sugar, whose active mass and concentration are constant and identical, for it is found that at a fixed temperature one cubic centimetre of a saturated aqueous solution of sugar always contains the same weight of sugar. This side of the question will be very important when we come to discuss the conditions under which substances can be precipitated from solution.

Kinetic Order of Reaction.—We have seen that the equilibrium constant K can be regarded as the ratio of the velocity constants k_2 and k_1 for the backward and forward reactions respectively:

$$K = k_2/k_1.$$

This relation, however, affords no information concerning the individual values of either k_1 or k_2. Nor can we assume that for a reaction stated as

$$nA + mB + pC \rightarrow \text{products}$$
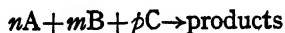
the reaction velocity found in experiment will agree with such an expression as

$$\text{Rate} = k[A]^n[B]^m[C]^p$$

We are again faced with the question of mechanism of reaction already touched on above. Consider the reaction in aqueous solution between hydrogen peroxide and hydriodic acid, expressed by the equation

$$2HI + H_2O_2 = 2H_2O + I_2 \qquad (1)$$
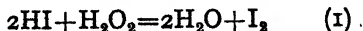
Experiment proves conclusively that the rate of production of iodine is accurately given by the equation

$$\text{Rate} = k[HI][H_2O_2] \qquad (2)$$

while a naïve interpretation of equation (1) might suggest

$$\text{Rate} = k[HI]^2[H_2O_2] \qquad (3)$$

Detailed investigation shows that the changes actually occurring are as follows:

$$HI + H_2O_2 = HIO + H_2O \qquad (a)$$
$$HIO + HI = I_2 + H_2O \qquad (b)$$
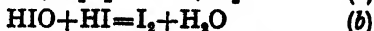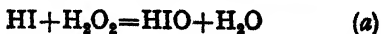
the stage (a) being very much slower than the stage (b). In these circumstances we see that the over-all rate of the reaction will be governed almost exclusively by (a), and equation (2) is explained, and equation (3) rejected. It may easily be understoʼ why the reaction does not pursue the course indicated by the single equation (1). This mode of reaction would require the simultaneous collision of three molecules, an event enormously less frequent than a binary collision.

In general for a reaction expressed stoichiometric by the equation

$$nA + mB = \text{products},$$
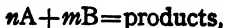
we find for the rate of reaction (by observing how the rate depends on concentration)

$$\text{Rate} = k[A]^a.[B]^b,$$

where a and b are commonly but not necessarily integers, which may have the values, 2, 1, or 0. The sum $a+b$ only rarely exceeds 2. If an index is zero it of course means that the concentration concerned is effectively constant during the reaction. This may come about in various ways, for example:

(1) The reagent is present in great excess (p. 118);
(2) The reagent is present as a solid, giving constant vapour pressure, or a fixed concentration in (saturated) solution (p. 114);
(3) The reagent is a *catalyst* (p. 213).

The sum $a+b$ is termed the *total kinetic order* of the reaction, while a single index such as a is called the *order in respect to* A, etc. While in a number of simple reactions it may emerge from experimental study that $n=a$, and $m=b$, it must be strongly emphasized that in general the kinetic order cannot be deduced from the ordinary stoichiometrical equation, but must be sought in experiments designed to reveal it. Not infrequently it may be found that one or more of the products may adversely affect the progress of the forward reaction (*see* p. 217). The concentration of such an ' inhibitor ' will appear in the expression for the rate with a *negative* index, i.e. in the denominator:

$$\text{Rate} = k[A]^a.[B]^b/[P]^p.$$

Some confusion exists in the terminology of this subject. Referring again to the reaction

$$2HI + H_2O_2 = 2H_2O + I_2$$
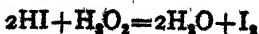
we might logically use the description *termolecular*, since clearly three molecules are involved in the complete reaction. On the other hand, as we have seen, the total order is only two, and on this account the description *bimolecular* is often preferred, though somewhat illogically. The need for a clear distinction between kinetic order and the total number of reacting molecules was sharpened by the discovery of true unimolecular reactions, of the type A=products. Before this it was customary to use ' unimolecular ' as synonymous with first kinetic order, even in cases where it was quite clear that more than one species participated, in a reaction wherein only one concentration changed. This latter type of reaction is now often termed ' pseudo-unimolecular.'

Unimolecular Reactions.—Unimolecular reactions are much less common than might be expected. Until 1925 only one homogeneous unimolecular gas reaction was known, the decomposition of nitrogen pentoxide in accordance with the equations:

$$N_2O_5 \rightarrow N_2O_3 + O_2$$
$$N_2O_3 \rightarrow NO + NO_2$$
$$NO + N_2O_5 \rightarrow 3NO_2.$$
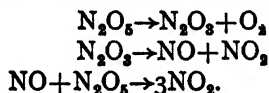
The last two reactions are incomparably faster than the first, which therefore determines the rate of the whole series.

This is another example of a phenomenon already mentioned above, the only velocity we are usually able to measure being the slowest of a series, and changes that take place comparatively rapidly will elude our observation.

When a quantitative study of the rate of decomposition of nitrogen pentoxide is made at a constant temperature, it is found that in unit time, say a second, a fixed proportion of the total weight of nitrogen pentoxide present at that moment suffers decomposition. When one-half of it has decomposed the rate of reaction has only half the value it had at the beginning of the change, and the reaction velocity gradually decreases until it becomes altogether imperceptible and no more pentoxide remains. The fraction of the total weight transformed per second is independent of the pressure or concentration of the gas, and if at any time during the change the gas is compressed or allowed to expand, the rate of formation of the products in grams per second is quite unaffected. Nor is the velocity affected by diluting the gas with nitrogen or argon. Indeed, so little does the tendency to decomposition of a nitrogen pentoxide molecule appear to depend on its surroundings that when the gas is dissolved in organic solvents the rate of decomposition is approximately the same.

At this point it will be as well to clear up a possible misunderstanding of the statement that the reaction velocity is independent

of the concentration. If the same weight of pentoxide is dissolved in various volumes of, say, carbon tetrachloride the products will be formed in each solution at an equal rate in grams per second. On the other hand, if various weights of nitrogen pentoxide are dissolved in equal volumes of carbon tetrachloride the rate of formation of the products in grams per second will not be the same in each solution, but will be proportional to the original concentration of each solution. The difference is only a matter of words, but it sometimes causes confusion. If at any time x gram-molecules of nitrogen pentoxide are present in V molecules of solvent, the rate of decomposition is, by the principle of mass-action, given by

$$-\frac{\mathrm{d}(x/V)}{\mathrm{d}t}=k(x/V);$$

but this equation is clearly equivalent to

$$-\frac{\mathrm{d}x}{\mathrm{d}t}=k(x)$$

(*See further*, p. 119).

In recent years a number of homogeneous first-order gas reactions have been investigated, notably by HINSHELWOOD and his collaborators. The majority consist of the decomposition of a comparatively complex organic molecule, e.g. diethyl ether, acetone, or aldehydes, but none shows the simplicity of the decomposition of nitrogen pentoxide, which at present stands alone in this respect. Unimolecular gas reactions will be further considered in Chapter VII in connection with the energy-changes involved.

Pseudo-unimolecular Reactions.—Though not unknown, homogeneous unimolecular reactions are likewise uncommon in the liquid phase. Many apparently unimolecular reactions appear to be so only because all the reactants except one are present in large excess. Thus if hydrogen peroxide is added to a large excess of acidified potassium iodide the following reaction takes place:

$$H_2O_2+2KI+2HCl\rightarrow2KCl+2H_2O+I_2,$$
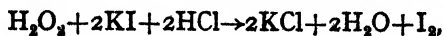
and the progress of the change can be followed by estimating at intervals the iodine liberated. This was one of the first reactions whose velocity was accurately measured (HARCOURT and ESSON, 1866). Under the conditions named the reaction appears to be unimolecular, but this is only because the active masses of the iodide and acid are so large when compared with the active mass of the peroxide that they can be regarded as constant throughout the experiment; the order in respect to these reagents is zero. If one of the reactants of a bimolecular reaction is in large excess, the reaction will for this reason appear to be unimolecular. This is a

common feature of reactions in fairly dilute aqueous solution in which the water itself plays a part, that is, in hydrolyses. Take as an example the hydrolysis of an ester such as ethyl acetate:

$$CH_3.COOC_2H_5 + H_2O \rightleftharpoons CH_3.COOH + C_2H_5.OH$$
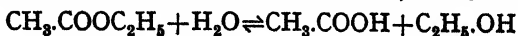
Under the conditions in which the measurements are usually carried out there is twenty or thirty times as much water as ester in the mixture, and the active mass of the water suffers no appreciable variation throughout the experiment. The early stages of the hydrolysis, before the back reaction begins to make itself felt, are therefore unimolecular, or appear to be so. The back reaction is bimolecular, and the change proceeds until the expression

$$\frac{[CH_3.COOH]\ [C_2H_5.OH]}{[CH_3.COOC_2H_5]}$$

attains a definite constant value. This equilibrium value will be the same whether we start with ester and water or with a dilute solution of ester, acid, and alcohol in any proportions, provided always that the water is present in large excess.

Velocity Equation for a Unimolecular Reaction.—The course of a unimolecular reaction lends itself very readily to mathematical expression. Consider the decomposition of nitrogen pentoxide. Let a be the weight of pentoxide originally present, and x the weight present after a time t measured from the beginning of the reaction. Then the rate of reaction is $-\dfrac{dx}{dt}$ (the negative sign means that x decreases with time), and as we find it to be proportional to x, we may put:

$$-\frac{dx}{dt} = kx,$$

where k is a constant. Hence:

$$-\frac{dx}{x} = k.dt, \text{ or } kt = -\log_e x + \text{integration-constant.}$$

To find the integration-constant we remember that at the beginning of the reaction t was 0 and x was equal to a. The integration-constant is found by substituting these values in the equation, and is equal to $\log_e a$, so that:

$$kt = \log_e a - \log_e x = \log_e \frac{a}{x}.$$

This *exponential relation* is typical of unimolecular reactions. An example of the application of this equation to a series of observations will be found in the Appendix to this chapter. Note that when x is zero t is infinite, so that no unimolecular reaction ever

comes to an end, but in practice a time can always be found after which the remaining reactant is present in such minute quantity as to be undetectable. It is, however, important to remember that there is no definite time after which the reaction is finished. If it be desired to express the reaction velocity in some such way, the 'half-life period' is calculated. This is the time at which one-half of the reactant originally present has been decomposed, and is a perfectly definite quantity.

At this point
$$x = \frac{a}{2}$$

and
$$kt = \log_e 2,$$

so that
$$t = \frac{1}{k} \cdot \log_e 2.$$

The half-life period is therefore inversely proportional to the velocity-constant k. It should be remembered that the unimolecular reaction-velocity equation, in agreement with experience, contains no term referring to concentration.

Bimolecular Reactions.—Homogeneous reactions are in large majority bimolecular. It appears that most reactions are brought about by the collision of two molecules, and as previously suggested the predominance of bimolecular reactions over those of higher order is due to the relative improbability of three or more molecules coming into contact at the same time. As an example of a bimolecular reaction we may take the decomposition of nitrous oxide:
$$2N_2O \rightarrow 2N_2 + O_2.$$
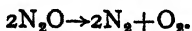
If nitrous oxide be confined at a high but constant temperature in a vessel fitted with a manometer, the pressure will be observed gradually to rise until it attains a value 50 per cent greater than its initial value. At this point the reaction is complete, since the number of molecules in the system is 50 per cent greater at the end than at the beginning. The rate at which the pressure increases is a measure of the rate at which the nitrous oxide decomposes. Let x be the fraction decomposed at a time t measured from the beginning of the reaction, and let the pressure at this moment be p, while p_0 was the pressure at the beginning of the reaction. Then:

$$\frac{p}{p_0} := \frac{\text{number of molecules present at time } t}{\text{number of molecules present at beginning}} = \frac{(2-2x)+3x}{2} = 1 + \frac{x}{2}.$$

Hence $x = 2\left(\frac{p}{p_0} - 1\right)$.

If now the pressure be plotted against the time, $\frac{dp}{dt}$ can be

measured for various values of p and t, and $\dfrac{dx}{dt}$ can be calculated from it by the relation:

$$\frac{dx}{dt}=\frac{dp}{dt}\cdot\frac{dx}{dp}=\frac{2}{p_0}\cdot\frac{dp}{dt}.$$

This gives us the rate of decomposition at any moment, and we can see how it varies with x. If the decomposition is bimolecular:

$$\frac{dx}{dt}=k.(1-x)^2,$$

and it is found that this equation does truly express the rate of change. When different numbers of molecules appear on either side of a gas reaction its course can be most easily followed by noting the rate of change of the pressure. When this is not so, as for instance in the reaction:

$$CO_2+H_2\rightleftharpoons CO+H_2O,$$

the velocity must usually be determined by analysis at fixed intervals.

As an example of a homogeneous gaseous termolecular reaction we may quote the formation of nitrogen dioxide from nitric oxide and oxygen:

$$2NO+O_2\rightarrow 2NO_2.$$
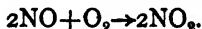
The rate of formation of nitrogen dioxide at any moment is given by the equation:

$$\frac{d[NO_2]}{dt}=k[NO]^2[O_2].$$

Rapid Consecutive Reactions.—An interesting reaction taking place in solution is that usually written:

$$\underset{\substack{\text{thiocyanic}\\\text{acid}}}{HSCN}\ +\ 3H_2O_2\ \rightarrow\ \underset{\substack{\text{hydrocyanic}\\\text{acid}}}{HCN}\ +\ H_2SO_4\ +\ H_2O.$$
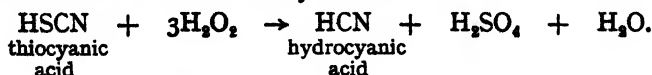
It might be supposed that this reaction is quadrimolecular. The velocity is, however, found to be proportional to

$$[HSCN]\,[H_2O_2]^2,$$

so that the reaction which determines the velocity appears to be:

$$HSCN+2H_2O_2\rightarrow HCN+2H_2O+SO_2.$$

The sulphur dioxide would then be oxidized by a further molecule of hydrogen peroxide:

$$SO_2+H_2O_2\rightarrow H_2SO_4.$$

This second change has been shown by experiment to be much more rapid than the first, and has no effect on the observed velocity of

the total change, which is therefore termolecular. This again illustrates the difference that may be found between the observed order of a reaction and the order suggested by the equation. Reactions of higher order than the third are very rare.

When the results of an investigation of reaction velocity show the reaction to follow a course other than that required by the ordinary equation, it is usually easy to devise a series of reactions to fit the observed facts. But in so doing caution must be exercised, and it must be shown that reactions supposed to take place rapidly actually do so in fact. Hypothetical intermediate products should if possible be isolated and their reactions studied. In the thiocyanic acid oxidation which has just been mentioned these precautions have been observed, and experiment shows that sulphur dioxide really is rapidly oxidized to sulphuric acid by hydrogen peroxide. Neglect of such precautions has led to much faulty theorizing.

Effect of Pressure.—At this stage it will be as well to consider in general terms the effect on the equilibrium of changes of pressure or volume. Let a gaseous system be in equilibrium, and let the pressure on it be increased. Then we know from Le Chatelier's principle that the equilibrium will, if possible, shift in such a way as to oppose the increase of pressure. To see how this comes about let us consider the gaseous system

$$2NO_2 \rightleftharpoons 2NO + O_2,$$

formed from pure NO_2 at a constant temperature, and under a total pressure P. Then if p_1 and p_2 are respectively the partial pressures of nitrogen dioxide and oxygen, the partial pressure of nitric oxide is $2p_2$. Hence $p_1 + 3p_2 = P$. Since, by Boyle's law, the concentration of a gas, in gram-molecules per c.c., is proportional to its partial pressure, the existence of equilibrium requires, by the law of mass-action (p. 113),

$$(2p_2)^2 \cdot (p_2)/(p_1)^2 = 4p_2^3/p_1^2 = K.$$

Let the total volume of the system be now halved by a sufficient increase in the total pressure. If no chemical change occurred the required pressure is, by Boyle's law, equal to $2P$, and since all partial pressures would be doubled, the equilibrium would require

$$(4p_2)^2 \cdot (2p_2)/(2p_1)^2 = K' = 2K.$$

But K must remain unchanged since the temperature is constant. Hence a chemical change must take place, reducing K' to K, i.e. increasing p_1 at the expense of p_2, which means the formation of nitrogen dioxide from nitric oxide and oxygen. Since this change reduces the total number of molecules in the system, the actual pressure will sink below $2P$. Le Chatelier's principle is thus operative, to annul partially the increase of pressure expected by

Boyle's law to achieve a given decrease of volume. The effect of an increase of pressure on a gaseous system in equilibrium is thus in general to cause, *if possible*, a shift of the composition of the gaseous mixture towards one occupying a lesser volume, or, more simply expressed, a reduction in the total number of molecules in the system. Decrease of pressure has the opposite effect.

In gas reactions in which equal numbers of molecules appear on each side of the equation, alterations of pressure have no effect on the equilibrium. An example is furnished by the decomposition of hydrogen iodide, and we have already seen that the equilibrium equation need contain only the weights of reactant and products, since V can be cancelled in the final expression.

The effect of alterations of pressure can be quantitatively deduced from the equilibrium equation, since the equilibrium constant K, though dependent on temperature, is independent of the pressure. The technically very important synthesis of ammonia will serve as an example. At a given temperature let the partial pressures of nitrogen, hydrogen, and ammonia at equilibrium be a_0, b_0, and c_0. Then

$$\frac{a_0 . b_0{}^3}{c_0{}^2} = K.$$

Now let the pressure on the system be doubled. To simplify the calculation let us assume, as is always the case in technical practice, that the partial pressure of ammonia is small compared with the partial pressures of the nitrogen and hydrogen. Then when the total pressure is doubled the partial pressures of nitrogen and hydrogen at equilibrium (we will call the new equilibrium partial pressures a_1, b_1, and c_1) will also be approximately doubled, since we can neglect the decrease due to the formation of more ammonia. Then:

$$\frac{a_1 . b_1{}^3}{c_1{}^2} = K = \frac{2a_0 . (2b_0)^3}{c_1{}^2}.$$

$$c_1{}^2 = \frac{16 . a_0 . b_0{}^3}{K} = \frac{16 K c_0{}^2}{K} = 16 c_0{}^2. \qquad c_1 = 4c_0.$$

We see that the partial pressure of ammonia has been quadrupled by the increase of pressure, while the partial pressure of the reactants has only been doubled. The fractional yields of ammonia from nitrogen are equal to $\frac{2c_0}{a_0}$ and $\frac{2c_1}{a_1}$, and since $c_1 = 4c_0$ and $a_1 = 2a_0$ the second fractional yield is twice the first. By doubling the pressure we have therefore doubled the fractional yield of ammonia, and it can easily be shown that if the fractional yield of ammonia is small it is directly proportional to the total pressure on the

system. The commercial synthesis of ammonia is in fact only made possible by the use of very high pressures, as we shall see when we come to discuss the process in detail (p. 388).

Concentration of the Reactants.—When a reaction is being carried out with the object of securing the product in maximum yield, there must be chosen not only the best temperature and pressure but also the most suitable proportion between the reactants. In a reversible reaction the best yield from all the reactants is always obtained from the mixture in equivalent proportions. Thus in the synthesis of ammonia both nitrogen and hydrogen have to be artificially prepared, and economical working requires that they should be mixed in the proportion of one volume of nitrogen to three of hydrogen. As is common in industrial practice, the gases are not allowed to reach a stage of approximate equilibrium, since this would take inconveniently long. The mixed gases are therefore allowed to leave the reaction chamber before the equilibrium concentration of ammonia has been reached, and the ammonia is removed at a lower temperature. The remaining nitrogen and hydrogen, which are still in the correct proportions, are then mixed with fresh gas and again passed through the reaction chamber, and so the cycle goes on. By the removal of one of the products a reversible reaction can be made to go to completion, but if the yield of each operation is very small the process may become too slow to be economic.

In reactions where one reactant, such as water or air, is very much more abundant than the others, the best yield from the practical point of view is usually obtained by having this reactant present in excess. Consider as an example the oxidation of sulphur dioxide by atmospheric oxygen in the contact process for the manufacture of sulphuric acid:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$
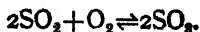
The action is reversible and it can be shown from Le Chatelier's principle or from the equilibrium equation that the formation of the trioxide is favoured by high pressure. It can likewise be shown that at a given temperature and total pressure the percentage yield of sulphur trioxide can be indefinitely improved by increasing the partial pressure of oxygen as compared with the partial pressure of sulphur dioxide in the reaction mixture. From the point of view of economy the percentage conversion is the important factor, since the sulphur dioxide must be obtained by burning sulphur or sulphur-containing materials, while the air costs nothing. On the other hand, if the air is in very large excess, time and energy will be expended in pumping through the system a gaseous mixture containing only a small fraction of sulphur dioxide. An intermediate

proportion must therefore be chosen which approximately satisfies both conditions.

Inhibition of Reactions.—An interesting example of inhibition, and of the type of explanation that may be advanced, can be found in the very important reaction occurring in the nitration of aromatic hydrocarbons. In the case of the nitration of benzene, C_6H_6, the net reaction can be written in the equation $C_6H_6+HNO_3=C_6H_5NO_2+H_2O$, but abundant experimental evidence has accumulated that the actual nitrating agent is not molecular nitric acid but the so-called nitronium ion $(NO_2)^+$ derived from it. When the acid is concentrated or is dissolved in organic solvents it undergoes an unexpected form of ionization, according to the equations:

$$HNO_3 \rightleftharpoons NO_2^+ + OH^-$$
$$HNO_3 + OH^- \rightleftharpoons H_2O + NO_3^-,$$
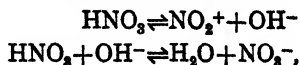
which may be summed in the form

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$
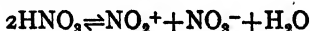
It is thought that this equilibrium is rapidly established, but the ensuing reaction between the hydrocarbon and the nitrating agent is relatively slow; the rate of this reaction is determined, for a given concentration of hydrocarbon, by the concentration of the cation NO_2^+. It is however readily seen that the addition of nitrates, i.e. NO_3^- ion, to the reaction mixture, must, by driving the equilibrium in which it is present to the left, adversely affect the concentration of the cation NO_2^+. It is found, in complete accordance with this theory, that the rate of nitration by nitric acid in organic solvents is inversely proportional to the concentration of nitrate ion.

The reader will perhaps be interested to deduce, on the lines of the above argument, from equation (2) on p. 113 the known fact that the product hydrogen bromide restrains the rate of its formation from molecular hydrogen and bromine, and to convince himself that no such restraint will operate on the combination of hydrogen and iodine.

Reactions in the Human Body.—Health depends on the delicate balance between numerous reactions which take place in the human body, and to preserve this balance a constant temperature is necessary. The body is a highly efficient thermostat, operating with a normal variation of less than half a Centigrade degree over a range of conditions which few artificial thermostats are required to suffer. Heat is supplied by oxidation processes, and is dissipated by evaporation from the skin. The rate of cooling can be increased if necessary by perspiration, but if the atmosphere is nearly saturated with water the process is not very effective, as evaporation

takes place very slowly in these conditions. This is why a hot, humid climate is so difficult to bear.

If the thermostatic arrangements fail, the chemical equilibria in the body are disturbed and the patient becomes ill.

APPENDIX TO CHAPTER III

Observations on a Unimolecular Reaction.—In the presence of an excess of a strong acid, bromine water reacts with formic acid according to the equation:

$$Br_2 + H.COOH = 2HBr + CO_2 \uparrow .$$
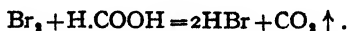
If the formic acid is in large excess in comparison with the bromine, the reaction appears to be unimolecular.

In the following experiment a solution of sodium formate and hydrochloric acid was mixed with dilute bromine-water. Before and
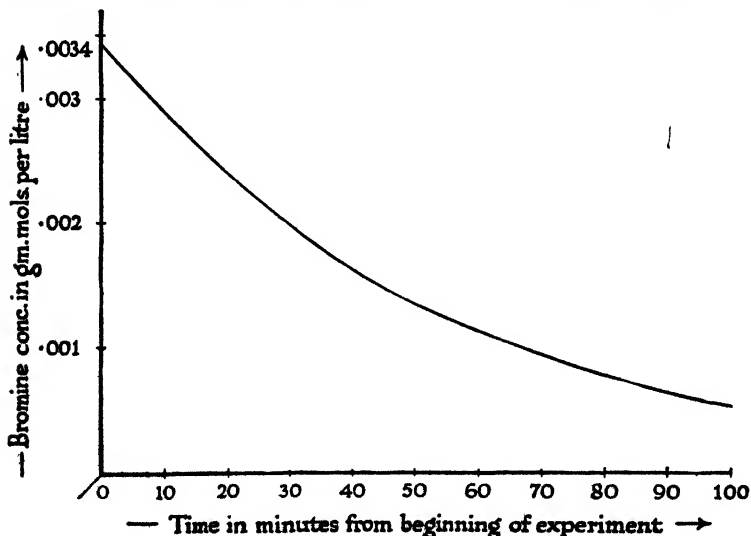
FIG. 27. COURSE OF A UNIMOLECULAR REACTION

after mixing, the solutions were kept in a thermostat at 18°. The initial concentrations of the mixture were: sodium formate, 0.2 molar; hydrochloric acid, 3 molar; bromine .0034 molar (i.e. .0034 gram-molecules of Br_2 per litre). The initial volume of the mixture was 500 c.c., and at ten-minute intervals from the time of mixing (at which $t = 0$), 50 c.c. portions were withdrawn and analysed for free bromine by addition to excess of potassium iodide solution followed by titration against sodium thiosulphate. The table shows the results obtained:

Time in Minutes	Bromine Concentration (gram-molecules per litre)	$\log_{10}\dfrac{\cdot 0034}{x}$	$k = \dfrac{1}{t}\log_{10}\dfrac{\cdot 0034}{x}$
t	x		
0	0·00340	0	
[10	0·00297	0·0587	0·0059]
20	0·00241	0·1498	0·0075
30	0·00197	0·2368	0·0079
40	0·00166	0·3114	0·0078
50	0·00139	0·3885	0·0078
60	0·00114	0·4746	0·0079
70	0·00096	0·5492	0·0078
80	0·00075	0·6564	0·0082
90	0·00065	0·7186	0·0080
100	0·00053	0·8072	0·0081

It is obvious that the value of k is approximately constant. In the diagram (Fig. 27) the bromine concentration is plotted against the time. Since the reaction never comes completely to an end, the curve is asymptotic to the axis of time.

SUGGESTED FOR FURTHER READING

HINSHELWOOD: *Kinetics of Chemical Change in Gaseous Systems. Kinetics of Chemical Change* (1940).

MOELWYN-HUGHES: *Kinetics of Reactions in Solution* (1947).

CHAPTER IV

THE NATURE OF SOLUTION

Solutions.—The idea of solutions is familiar to every student of chemistry. Inorganic chemistry is in the main the study of fluids, and it is usually so much easier to dissolve a substance than to vaporize it that solutions play a predominant part.

In this chapter we shall consider only liquid solutions, in which the *solute* or dissolved substance may be a solid, liquid, or gas. There is no rigid distinction between homogeneous mixtures of two liquids and a solution of one in the other, but it is usual to speak of solutions only when one constituent is present in large excess. For example 95 grams of water and 5 grams of alcohol may properly be called a solution of alcohol in water, 50 grams of each is a mixture of water and alcohol, and 5 grams of water and 95 grams of alcohol is a solution of water in alcohol. Most of the solutions with which we have to deal in inorganic chemistry are aqueous solutions, not only because water is the most abundant solvent but also because it is the only one in which most inorganic compounds are sufficiently soluble. It is for this reason that the properties of aqueous solutions are of such immense importance to the chemist, and why their better elucidation in the course of the last forty or fifty years has been of so great a service to science.

Solubility.—The phenomenon of saturation is so well known that it need not trouble us here. From the earliest times it has been

understood that a given mass or volume of solvent cannot dissolve more than a fixed weight of solute at a given temperature. By evaporating the solution or by cooling it this weight may often be exceeded, but the solution is then in an unstable state of supersaturation and by various devices can be made to deposit the whole excess of solute over the fixed weight. This deposition may be brought about by shock, or by introducing into the solution a fragment—the minutest particle is enough—of the solid solute or of a crystal isomorphous with it. The result of this process, which is called *seeding* or *inoculation*, is that crystals grow out from the solid particle. It is often possible to prepare solutions—for example those of calcium nitrate—so supersaturated that on inoculation they set solid. The weight of solute in unit weight or volume at a given temperature in equilibrium with excess of solute is called the *solubility* at that temperature: in other words, *solubility* is the composition of the saturated solution. Solubilities must always be measured in the presence of excess of the solute, as there is otherwise no means of making sure that the solution really is saturated, and sufficient time must always be allowed—it is often surprisingly long—to allow equilibrium to be established. At this point as much solute enters the solution as leaves it, and the concentration of the solution therefore remains constant. Solubilities can be expressed in at least four ways, and it is important when referring to them to make it quite clear which is intended. Using grams and litres the principal ways are:

1. Grams solute per ml., 100 ml., or litre of solution.
2.   „   „   „ gm., 100 gm., or 1000 gm. of solution.
3.   „   „   „ ml., 100 ml., or litre of solvent.
4.   „   „   „ gm., 100 gm., or 1000 gm. of solvent.

Of these the first is usually the best, because for ordinary work solutions are usually made up by volume and the solubility is then a direct measure of the weight of solute required. To convert 1 to 2 or vice versa the density of the solution must be known, and to convert 3 to 4 or vice versa the density of the solvent. To convert 1 or 2 to 3 or 4 we must know the change of volume on adding the solute to the solvent. These distinctions are specially important in concentrated solutions, and such an expression as ' a 20-per-cent solution ' should never be used in exact work, as it may be misinterpreted.

Effect of Temperature.—The process of solution is always attended by either the liberation or absorption of heat. From Le Chatelier's principle we know that the solubility of substances that absorb heat when they dissolve will increase with temperature, whereas

the reverse is true of substances that give out heat on solution. Most substances belong to the first class, and are more soluble in
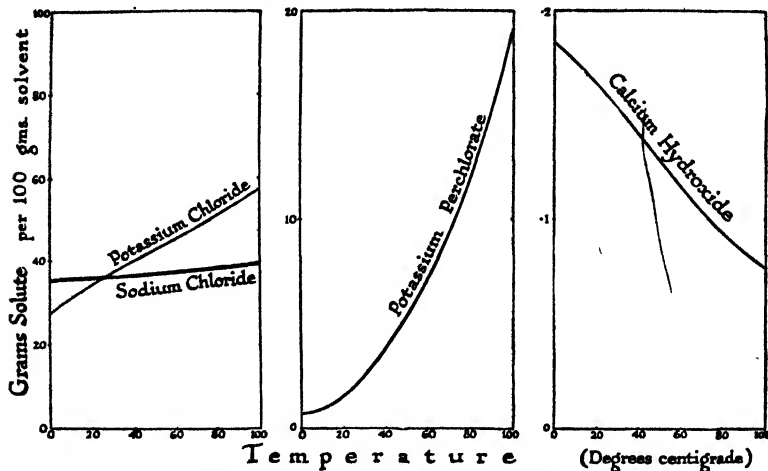
FIG. 28.   TYPICAL SOLUBILITY CURVES

the hot solvent.   Examples of both types are shown in Fig. 28. The behaviour of some substances is more complicated, and their solubility curves, that is, the curves obtained by plotting solubility
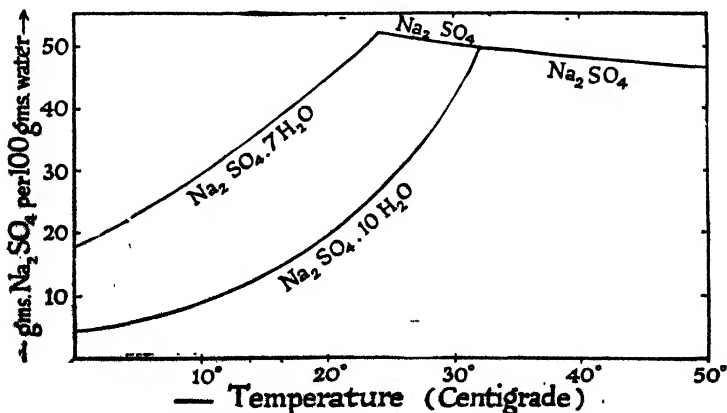
FIG. 29.   SOLUBILITY OF SODIUM SULPHATE

against temperature, show abrupt changes of direction. These breaks in the curve are due to the formation of compounds between solvent and solute which exist only between definite limits of

temperature.   Sodium sulphate is one of the best examples of this
behaviour, and its solubility curve is shown in Fig. 29.   Above
32° only the anhydrous salt crystallizes from sodium sulphate
solutions, the hydrates being incapable of existence above this
temperature.   The anhydrous salt has a negative temperature-
coefficient of solubility.   Below 32° two hydrates can exist, having
the formulae $Na_2SO_4.7H_2O$ and $Na_2SO_4.10H_2O$, the former being
the more soluble.   If a solution of sodium sulphate is quickly
cooled to a temperature at which it is supersaturated with respect
to these hydrates, either may appear in the solid state, but the
heptahydrate ($Na_2SO_4.7H_2O$) is precipitated more frequently than
the decahydrate.   It is nearly always found, in other systems as
in this one, that when the crystallization of two forms is possible,
the more soluble crystallizes first.   This principle governs spon-
taneous crystallization, but by inoculation with a crystal of the
desired substance supersaturated solutions of sodium sulphate can
be made to deposit either hydrate at will.   Inspection of these
curves shows that in stating solubility it is essential to name the
hydrate to which the measurements refer, i.e. the nature of the
solid phase in equilibrium with the solution.
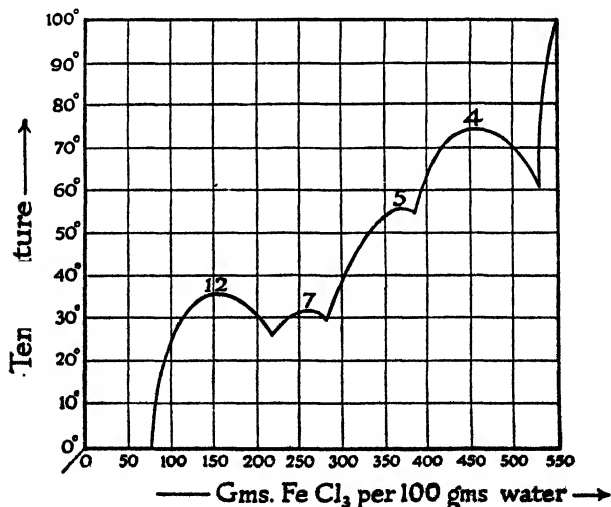
FIG. 30.   SOLUBILITY OF FERRIC CHLORIDE

Hydrates.—The equilibrium conditions between salts and their
solutions will be dealt with more fully when we come to the phase
rule (Chapter V), but brief allusion must here be made to the
behaviour of salts whose hydrates are stable at their melting-points.

When these hydrates are heated the salt dissolves in its own water of crystallization, and the solubility curve shows a maximum. Thus ferric chloride dodecahydrate (Fig. 30) melts at 37°; and at this temperature the solid hydrate is in equilibrium with an aqueous solution of ferric chloride of the same composition. The hydrate in the solid or liquid state behaves as a chemical individual, and its melting-point is depressed by the addition either of water or of the anhydrous salt. The other hydrates behave in a similar way, and on plotting the solubility of the anhydrous salt against the temperature we get the familiar cascade curve. The small figures above the maxima indicate the number of molecules of water associated with two molecules of ferric chloride.

In the evaporation of ferric chloride solutions a series of fusions and solidifications will be observed. As water is removed and the temperature rises each hydrate melts, and then solidifies as a mixture with the next hydrate when the water necessary to its existence has been driven off. Finally the last hydrate, $FeCl_3.2H_2O$, is broken down, and the curve rises sharply with no further breaks.

Solubility and Chemical Composition.—No general quantitative law is known connecting the solubility with the other properties of solvent and solute, and this is perhaps not surprising in view of the number and complexity of the factors which influence solubility. The dielectric constant of the solvent, the stability of hydrates or other compounds between solvent and solute, and the molecular condition of the solute in solution, all come into play. Relations are known for particular groups of compounds, but they are entirely empirical and are subject to exceptions. As an example we may mention ABEGG's *Rule* that the solubility in water of the salts of the alkali-metals with strong acids decreases from lithium to caesium, while their salts with weak acids observe the reverse order. Sodium chloride, which over a considerable range of temperature is less soluble than potassium chloride, is an exception.

Solubility and Chemical Behaviour.—In spite of the difficulty of predicting it from theoretical considerations, the solubility of a substance in water is frequently of such importance as largely to determine its chemical behaviour. At equilibrium the concentration and consequently the active mass of a substance cannot exceed the solubility, and is a constant if the undissolved substance be present, so that in solutions it usually controls the course of any reaction taking place. For example, when solutions of silver salts and chlorides are brought into contact the immediate effect is the precipitation of the insoluble silver chloride. If a substance is insoluble in water it can usually be most readily prepared in a state of purity by precipitation, and the relative solubilities of salts can often be used for the purification of one or both. A good example is furnished

by the preparation of potassium salts from the Stassfurt deposits in Germany, which are believed to have been laid down by the evaporation of an inland sea. They consist chiefly of the chlorides of sodium, magnesium, and potassium, together with magnesium sulphate. The valuable constituents are the potassium salts, which are extracted by making use of the fact that in the neighbourhood of 100° sodium chloride is less soluble than potassium chloride. Sodium chloride is readily deposited from the mixed solution, leaving the potassium salt with a small proportion of sodium and magnesium salts, which can be still further reduced by crystallization and washing.

The solubility of gases decreases with rising temperature, and if a gas cannot be expelled from a solution by boiling it is probably combined with the solvent.

Recrystallization.—Recrystallization, perhaps the most commonly used of all methods of purification, requires the use of a solvent in which the solubility of the substance to be purified has a high positive temperature-coefficient. A saturated solution in the hot solvent is prepared, and as large a proportion as possible of the substance is recovered by cooling the solution and collecting the precipitate. The impurities remain in solution, as they are not present in sufficient quantity to form a saturated solution. Nevertheless some of the impurity usually finds its way into the precipitate, particularly if it is isomorphous with the substance to be purified, and as isomorphous substances are those most likely to occur as impurities, recrystallization is usually carried out more than once. If the substances form mixed crystals in all proportions, recrystallization as a means of purification is much reduced in value. The most serious disadvantage of the method is the loss of material entailed, and if the supply is limited it is worth while going to some trouble to find a solvent in which the temperature-coefficient of the solubility is sufficiently large to reduce the loss to a minimum.

Osmotic Pressure.—A fundamental property of solutions is the osmotic pressure, and though the difficulty of measuring it directly has been a bar to its practical use, yet its consequences are of the greatest practical importance. Osmosis was described by Du-TROCHET in 1726, and again in 1750 by the ABBÉ NOLLET, whose treatise on physics enjoyed a wide circulation in the eighteenth century. Nollet found that if water and spirit of wine were separated by a bladder, the water would pass through the bladder to dilute the spirit of wine, and if this was confined in a glass vessel would cause the bladder covering it to expand and burst. In 1867 chemical membranes were prepared for the first time by MORITZ TRAUBE, and were employed by the botanist PFEFFER in his famous series of measurements of osmotic pressure. He used a

membrane of copper ferrocyanide, precipitated within the pores of a clay vessel by filling it with a solution of potassium ferrocyanide and immersing the whole in a solution of copper sulphate. The improvements introduced by later workers included the passage of an electric current from one solution to the other while the membrane is being formed, and the use of higher pressures in forming the membrane.

Membranes which allow the passage of solvent but prevent that of dissolved substances are termed *semi-permeable* with respect to the solvent and solute. It is found that if a porous pot in which such a membrane has been precipitated be filled with, say, cane-sugar solution and immersed in water, then the water will pass into the pot through the membrane and will dilute the sugar solution. The latter will rise to a height that may reach several feet unless pressure be applied to it to prevent it. Theoretically the sugar solution will
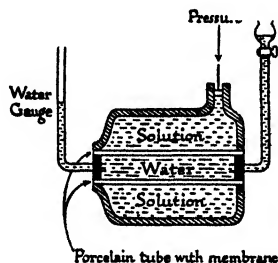
FIG. 31. BERKELEY AND HARTLEY'S APPARATUS (DIAGRAMMATIC)

rise to such a height that the osmotic pressure exactly balances the tendency to osmosis, but the difficulty of preparing membranes that will stand a large pressure on one side has prevented the general use of this method for measurement. To serve for an accurate determination of osmotic pressure a membrane must be perfect in two senses: (1) it must be macroscopically continuous without apertures, (2) it must be perfectly semi-permeable, i.e. it must be completely impervious to solute. One can hope to satisfy the first requirement by careful attention to detail in the preparation, but the second presents difficulties unsurmounted to the present. The facts are that for a direct measurement of the osmotic pressure of aqueous solutions there is only one possible solute—cane-sugar— and only one membrane—copper ferrocyanide. Other membranes are never perfectly semi-permeable to any simple solute in aqueous solution, while copper ferrocyanide is strictly impervious only to cane-sugar. Hence direct osmotic data, although now very full and accurate for the materials mentioned, are exceptionally meagre in respect to variety of solute or solvent. In the apparatus used by the EARL OF BERKELEY and E. G. J. HARTLEY, an external pressure

exactly sufficient to prevent motion of water through the membrane is applied to the solution. The osmotic pressure of the solution is then represented by the external pressure, and dilution of the original solution by the entry of water through the membrane is avoided. The membrane was precipitated in a porcelain tube (see diagram) which contained the solution and was enclosed in a cylindrical vessel containing water. Pressure was applied to a narrow tube connected with the solution until the liquid level in the narrow tube had no tendency either to rise or to fall; the pressure necessary to bring this about is the osmotic pressure. The chief advantage of this method of operation lies in the saving of time required to test the 'perfection' of a prepared membrane. If the membrane is defective it will not usually fail entirely to promote osmosis, but the pressure registered will fall short of the true pressure. Hence the only way to ascertain the true (maximal) pressure is to prepare and' test a number of membranes, and as, in the classical method of Pfeffer, the maximum pressure is very slowly reached, experiments by this direct method are extremely prolonged and tedious.

Vapour Pressure.—It is well known that the vapour pressure of solvent over solutions is lower than that over the pure solvent. The boiling-point of a solution (of non-volatile solute) is above that of the solvent, because the boiling-point is the temperature
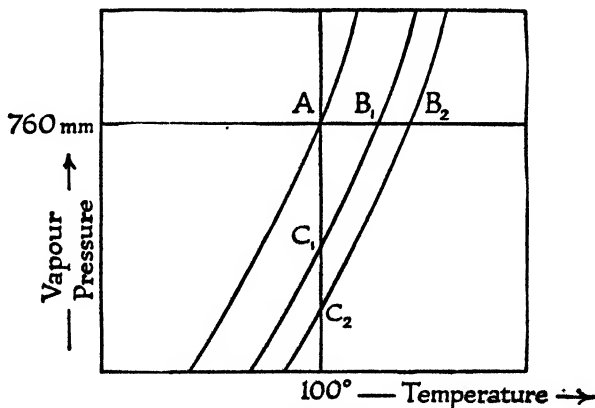
FIG. 32. VAPOUR PRESSURE AND THE BOILING-POINT

to which the liquid must be raised to make its vapour pressure equal to (standard) atmospheric pressure. The diagram (Fig. 32) shows the variation of the vapour pressure of water, and that of two aqueous solutions, with the temperature, the boiling-points being indicated by the points A, B_1, and B_2, where the curves

cross the 760-mm. mark. It is suggested by the diagram, and can be rigidly proved by thermodynamics, that for small concentrations AB is proportional to AC, that is, the rise in the boiling-point is proportional to the decrease of the vapour pressure. The same considerations apply to the lowering of freezing-point, and both conclusions have been abundantly verified by experiment. A mixture containing a total of n gm.-mols., of which $n + n_B$ are of the species A and n_B of the species B, may be regarded as derived from n gm.-mols. of A by the withdrawal of n_B of its mols., and their replacement by n_B gm.-mols. of B. On this simple view we should expect the vapour pressure of A to be reduced p_A to $p_A.n_A/(n_A + n_B) = p_A.N_A$. N_A is termed the *molar fra*   of A in the mixture. The same argument is applicable to   vapour pressure of the second constituent B. Hence we should have for the partial pressures p_A' and p_B' arising from the mixture

$$p_A' = p_A N_A = p_A(1 - N_B),$$
$$p_B' = p_B N_B = p_B(1 - N_A),$$

whence, if we express the reduction of vapour pressure by δp,

$$\delta p_A / p_A = N_B, \text{ and } \delta p_B / p_B = N_A.$$

The expression $\delta p/p$ is known as the *relative lowering of the vapour pressure*. If B is effectively non-volatile, then p_A' is the total vapour pressure over the solution. The truth of the above theory may be indirectly tested by tracing a relation between osmotic pressure and lowering of vapour pressure.

Calculation of Osmotic Pressure.— Consider a solution of a non-volatile solute in equilibrium with the pure solvent and communicating with it through a semi-permeable membrane which allows the solvent molecules to pass through it freely but cannot be penetrated by the solute (Fig. 33). The solution will rise above the level of the solvent to a height proportional to the osmotic pressure. Call this height h. Let p_1 and p_0 be the vapour pressure of the solvent and solution respectively, and d the density of the solution. Let d' be the density of the vapour.
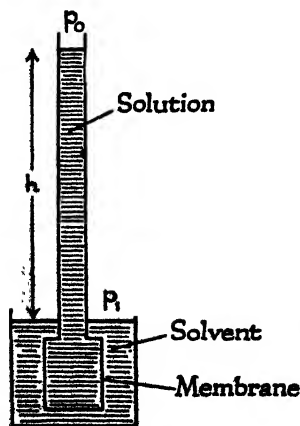
FIG. 33. VAPOUR PRESSURE AND OSMOTIC PRESSURE

If we assume that $p_1 - p_0 = \delta p$ is small enough for the variation of the vapour density d' in the vapour column to be

negligible, and that the vapour obeys the ideal gas law, then we have

$$hd' = \delta p, \quad pV = RT, \quad V = M/d', \quad \text{and} \quad hd = \Pi$$

where M is the molecular weight of the vapour, and Π the osmotic pressure. Together these equations give

$$\Pi/d = (RT/M)(\delta p/p) = (RT/M)N_A = (\text{constant})N_A.$$

This result may now be submitted to experimental proof by using the data on the osmotic pressure of aqueous solutions of cane-sugar collected in the table below. The first line, labelled m, gives the composition of the solution as gram-molecules of sugar per kilogram of *water*.

m	0·2	0·4	0·6	0·8	1·0
d (15°)	1·025	1·049	1·070	1·090	1·108
Π (atm., 15°)	5·03	10·03	15·27	20·72	26·42
Π/d	4·91	9·56	14·27	19·01	23·85
$(\Pi/d) \div m$	24·5	23·9	23 8	23·8	23·85

OSMOTIC PRESSURE OF CANE-SUGAR SOLUTIONS

The solutions shown in the table are sufficiently dilute for the quantity m, which is proportional to the *molar ratio* in the solution, to be set equal to the molar *fraction*, within the limits of error in the determinations of the osmotic pressure. The quotient in the last line shows by its constancy that our theoretical result is excellently confirmed.

When N_A becomes vanishingly small, the density d will be that of the pure solvent, and our expression for the osmotic pressure is easily shown to reduce to

$$\Pi V_s = RT,$$

where V_s is the volume of solution (or solvent) containing 1 gm. mol. of the solute. This simplified equation, strikingly analogous to the ideal gas law, may be used for an *approximate* calculation of the osmotic pressures of solutions more dilute than about 0·1 gm. mol. per litre. It is of interest to calculate, from the simplified equation, the osmotic pressures of the solutions given in the above table:

m	0·2	0·4	0·6	0·8	1·0
Π (obs.)	5·03	10·03	15·27	20·72	26·42
Π (calc.)	4·53	8·72	12·59	16·17	19·50

The very large errors must be ascribed to the falsity of the simple law, and not to a failure in the fundamental premises about the relative lowering of vapour pressure, for a constant and accurate estimate of the molecular weight of cane-sugar (342) is obtained from the freezing-points of *all* the above solutions (see below).

The following example will make clear the calculation of the

osmotic pressure of a solution of sufficient dilution. PFEFFER measured the osmotic pressure at 36° C. of a solution containing 9·99 gm. of sugar per litre of solution. Since the molecular weight of sugar is 342, the volume containing a gram-molecule of the solute is $\frac{342}{9\cdot99}$ litres=34·2 litres. As a consequence of the formal analogy between the gas law $pV=RT$ and the simplified osmotic law $\Pi V_s=RT$, the osmotic pressure is equal to the pressure of one mole of gas at 36° and occupying a volume of 34·2 litres, which is $\frac{22\cdot4\times(273+36)}{273\times34\cdot2}\times760=564$ mm. of mercury. The osmotic pressure found by experiment was 567 mm. of mercury—a difference of less than 1 per cent.

Freezing- and Boiling-points.—We have seen above (p. 135) that the depression of freezing-point, or the elevation of boiling-point, of a solution δT is proportional to the lowering of vapour pressure δp, and this in turn is proportional to the molar fraction of the solute A:

$$\delta T = k_1\delta p = k_2 N_A \text{ (k_1 and k_2 constants).}$$

If the solutions are dilute enough for these relations to hold, the approximation of setting $N_A=n_A/(n_A+n_B)$ equal to the *molar ratio* n_A/n_B will entail an error less than the probable error in the measurements of the boiling- or freezing-points. M_B being the molecular weight to be assigned to the solvent, and W_B its weight in grams, we have $n_B=W_B/M_B$. Hence we may write

$$\delta T = (k_2M_B).n_A/W_B.$$

Thus for a given weight of a given solvent B the value of δT depends only on the number of solute molecules, and not upon their chemical nature, a conclusion reached by RAOULT upon experimental grounds as early as 1882. For different solvents we see that

$$\delta T = K_B n_A/W_B \text{ (K_B a specific constant).}$$

The constant k_2 may be calculated by the methods of thermodynamics, and is then found to contain M_B in the denominator. Hence K_B, although of value specific to a solvent, does not in fact involve the molecular weight of the solvent.

The value of K_B can be found by experiments with solutes of known molecular weight, and the relation then applied to the determination of the molecular weights of other substances. It is important to remember that what we actually determine is the weight of the solute particle in terms of the hydrogen atom, and that this will only be the true molecular weight when the solute exists in solution in the form of single molecules.

The proportionality factor K_B varies from solvent to solvent, and is called the *molecular depression* of that solvent when measured in terms of the following units: 100 gm. of solvent and 1 gm.-mol. of solute. It is not strictly correct to define the molecular depression as the lowering of freezing-point produced in 100 gm. of solvent by the addition of 1 gm.-mol. of solute, since such a solution would be far too concentrated to obey the laws of dilute solutions, even supposing that the solute were soluble to this extent. An example will make the matter clear.

The molecular depression of water is 18·6°. A solution of 21·96 gm. of ethyl alcohol in 1000 gm. of water freezes at −0·826°. What is the molecular weight of ethyl alcohol?

Let the molecular weight be M. Then the solution contains $\dfrac{21\cdot96}{M}$ gm.-mols. of alcohol in 1000 gm. water, or $\dfrac{2\cdot196}{M}$ gm.-mols. in 100 gm. water. The depression of the freezing-point should therefore be:

$$18\cdot6 \times \frac{2\cdot196}{M} = 0\cdot826.$$

$$\therefore M = \frac{18\cdot6 \times 2\cdot196}{0\cdot826} = 49\cdot5$$

$$(C_2H_6O = 46).$$

Determination of Boiling-point.—The boiling-point of solutions is less frequently determined than the freezing-point because of experimental difficulties. A thermometer if placed in the vapour of the boiling liquid would register only the boiling-point of the solvent, and it must therefore be placed in the liquid, which is liable to become superheated. This difficulty can be avoided or minimized by some device which causes a very intimate mixture of the vapour with the boiling solvent. Of this type of device

Vapour from
boiling solvent

Hole

Bulb to catch spray

Thermometer

Graduated tube

Vapour exit

FIG 34. APPARATUS FOR MEASURING THE BOILING-POINT OF A SOLUTION

the Landsberger apparatus (Fig. 34) is the simplest, but has now given place to more compact forms of apparatus. The Landsberger apparatus is so contrived that the boiling solution is surrounded by

a vapour-jacket which prevents loss of heat to the air. Since vapour condenses in the solution, its initial and final volumes are not the same, and the tube is usually graduated so that the resulting dilution can be calculated.

Determination of Freezing-point.—The freezing-point of a solution can be measured with a high degree of accuracy. The apparatus used in the commonest method is shown in Fig. 35. The Beckmann thermometer is a differential instrument with a large thin-walled bulb, a long scale graduated in hundredths of a degree and covering only five or six degrees, and a mercury reservoir at the top which allows the mercury in the bulb to be augmented or diminished, so that the thermometer can be used for different solvents. With the help of a lens the temperature can be read to one-thousandth of a degree. When the thermometer has been set, the scale - reading corresponding with the freezing-point of the pure solvent is determined; some of the solute is then introduced through the side-tube and the new freezing-point measured. The solution may be made up to a fixed concentration by weight or volume, or its concentration may be determined by analysis after the experiment, as may be most convenient. An air-jacket separates the solution

FIG. 35.   APPARATUS FOR MEASURING THE FREEZING-POINT OF A SOLUTION

from the surrounding freezing-mixture. At the freezing-point the solution is in equilibrium with ice (or the solid solvent)—a point which will be more fully discussed in Chapter V—and when this point is reached the temperature remains constant for some time and can be noted.

In the second method, due to RICHARDS, a flask is filled with a mixture of the solution and finely-crushed solid solvent—e.g. ice —and surrounded by a freezing-mixture. The temperature drops to the point at which the solution is in equilibrium with the solid solvent—i.e. to the freezing-point—and remains steady there. A little of the solution is then withdrawn from the neighbourhood of the bulb of the thermometer and analysed.

Molecular Weight of Electrolytes in Solution.—These methods have been of great service in the determination of molecular weights, especially in organic chemistry. Many substances were found to

be associated in solution, that is, the molecular weight calculated in this way was found to be greater than that of the simple molecule. Thus acetic acid, $CH_3.COOH$, in benzene exists largely in the form of double molecules, as does benzoic acid, $C_6H_5.COOH$, in toluene. These results are not unexpected, and are often in agreement with the molecular weight of the vapour calculated from vapour-density measurements. But the behaviour of solutions that were good conductors of electricity, viz. solutions of strong acids and bases or of salts, was found to be anomalous. It was observed, for example, that the lowering of the freezing-point of water produced by adding a known small quantity of sodium chloride to it was very much greater than—in fact nearly twice as great as—similar measurements on organic solutes such as sugar would lead one to expect. VAN 'T HOFF, unable to account for these results by any experimental defect, was obliged to accept them as anomalous, and they received no satisfactory explanation till 1887, when by a single brilliant suggestion the young Swedish chemist ARRHENIUS reduced the subject to order. His theory of electrolytic dissociation is one of the great landmarks of chemical history, and is the basis of all modern work on solutions. Like many other theories which have now become familiar to us, it was in its day regarded as startling and strange, but though the first opposition was violent Arrhenius was able to support his ideas with so much evidence from experiment that in a few years they had become a recognized part of chemical knowledge. Since that time it has been necessary to modify the original conception in many important respects, and the theory has been exposed to much criticism, which though healthy has not always been well informed. This, however, it has survived, and later in the chapter we shall give a short list of the experimental evidence in its support. Our treatment of solutions throughout the book will be based on the modern form of the theory—which indeed is universally current—but the student should remember that what now appears comparatively simple may in later years reveal unsuspected complications. The more closely the experimental data are studied the more puzzling do some of them become. The dissociation theory provides us with a guiding principle, but we must often fall back on other considerations. The true test of the theory is its usefulness in interpreting the results of old experiments and predicting the results of new ones.

The Dissociation Theory.—ARRHENIUS suggested that when an electrolyte such as sodium chloride was dissolved in water it was at least partially dissociated into sodium and chlorine *ions*, consisting of atoms carrying equal and opposite electrical charges. The obvious criticism was raised that sodium could not exist in

the presence of water, with which, as is well known, it violently reacts; but it was pointed out that whereas sodium atoms react with water this does not prove that the same atoms would do so when electrically charged. The question of the charge on ions is intimately connected with work on the electrical conductivity of solutions, and the great success of Arrhenius's paper was due to the agreement he was able to produce between osmotic and conductivity work, so that before we can understand the real significance of dissociation we must deal with the behaviour of solutions under the electric current.

Faraday's Laws of Electrolysis.—This, like many other branches of electrical science, was first accurately investigated by FARADAY, and the principal results of his researches are embodied in his laws of electrolysis. These laws state that *the mass of any substance liberated by electrolysis is proportional to the electrical charge employed and to the chemical equivalent of the substance.* Their precise implication can best be understood from example.

Let a copper plate be immersed in a solution of copper sulphate and connected to the negative pole of a battery whose positive pole is connected to a platinum wire dipping in the solution, and let there be also included in the circuit a solution of silver nitrate with a silver cathode. When the current passes, silver and copper will be deposited on the cathodes at the expense of the electrolyte. From Faraday's laws we learn that the number of coulombs which pass is proportional to the weight of silver, and also to the weight of copper, deposited, so that a steady current will deposit a weight of metal proportional to the time for which it is allowed to flow. Further, the weight of copper to silver is in the ratio of the chemical equivalents of these metals, that is, $\frac{63 \cdot 6}{2}$ or 31·8 to 107·9. Similar deductions have been exhaustively tested by experiment and are found to be rigorously true. The theory of dissociation tells us why.

It is assumed that a solution of silver nitrate contains positively-charged silver atoms, or *silver ions*, and negatively-charged nitrate groups, or *nitrate ions*. They may be symbolized Ag^+ and NO_3^- or $Ag^{\cdot}$ and NO_3'. The positively-charged silver ions will be electrostatically attracted to the negative pole or cathode; when they reach it they give up their charge to the cathode and are converted to silver atoms which adhere to it. The passage of the current consists then, so far as the solution is concerned, of the transference of positive charges from the solution to the cathode; negative charges are simultaneously transferred to the anode from the solution, which therefore remains electrically neutral. If each silver ion carries the same charge, the weight of silver deposited will be

proportional to the total charge that passes round the circuit, in accordance with Faraday's law. The second part of the law will also be in agreement with theory if the copper ions (copper is bivalent) each carry twice the charge of the silver ions. It is also necessary that each copper ion should carry twice this unit charge if each of the negatively-charged ions in, say, a molecule of copper nitrate is to receive an equal unit charge of opposite sign.

Magnitude of the Ionic Charge.—If we calculate the value of this hypothetical unit charge a most significant value is obtained. The actual as well as the relative weights of atoms are known, and if we divide the number of coulombs required to deposit a given weight of metal by the number of atoms in the same weight of metal we can find the charge, in coulombs, carried by each atom or ion. In accordance with Faraday's law this value is the same for all univalent ions, but twice this value for bivalent ions, and so on. Its magnitude for univalent ions is $1 \cdot 602 \times 10^{-19}$ coulombs, a charge precisely equal to that obtained by physical methods and calculations as the charge of the electron, or unit particle of negative electricity. It follows that an atom is converted into an ion by the addition or removal of electrons in number equal to the valency of the atom. Thus in silver nitrate the silver atom has transferred one electron to the nitrate group; the silver ion consequently has a unit positive charge and the nitrate ion an equal negative charge. In copper nitrate the copper atom has lost two electrons, one to each of the nitrate groups, and therefore carries twice the charge of the silver atom.

The charge necessary to deposit a gram-equivalent of a metal from its solutions is called a *faraday*; it is equal to 96,490 coulombs, and its symbol is *F*.

Osmotic Effect of Electrolytes.—An ion, like an undissociated molecule, is effective in producing an osmotic pressure, and in lowering the freezing- or raising the boiling-point of a solution; so that if the molecular weight of a dissociated solute be determined by the freezing-point method it will appear lower than the formula weight. If the dissociation theory is correct, only those substances whose aqueous solutions conduct the electric current should give abnormal values for the molecular weight determined by the freezing-point method in water; and this is found to be so. By comparing the apparent with the true molecular weight it should be possible to calculate to what extent the substance is dissociated; we shall return to this point when we have more closely considered the process by which the current is carried.

Electrical Conductivity.—The power of a solution to conduct the current is determined by measuring its resistance in a Wheatstone's bridge in much the same way that we should measure the

conducting power of a metal. The solution is contained in a glass cell fitted with parallel plates, usually of platinum, and the whole is balanced against a known resistance in the other arm of the bridge. To avoid polarization an alternating current was used from a small

MEASUREMENT OF CONDUCTIVITY

Ground and greased joint (cap outside)

Mercury

Platinum plates coated with grey platinum

A

B

Greased joint

Thermostat water-level

Plates

SIMPLE ARRHENIUS FORM OF CONDUCTIVITY CELL

HARTLEY CONDUCTIVITY CELL
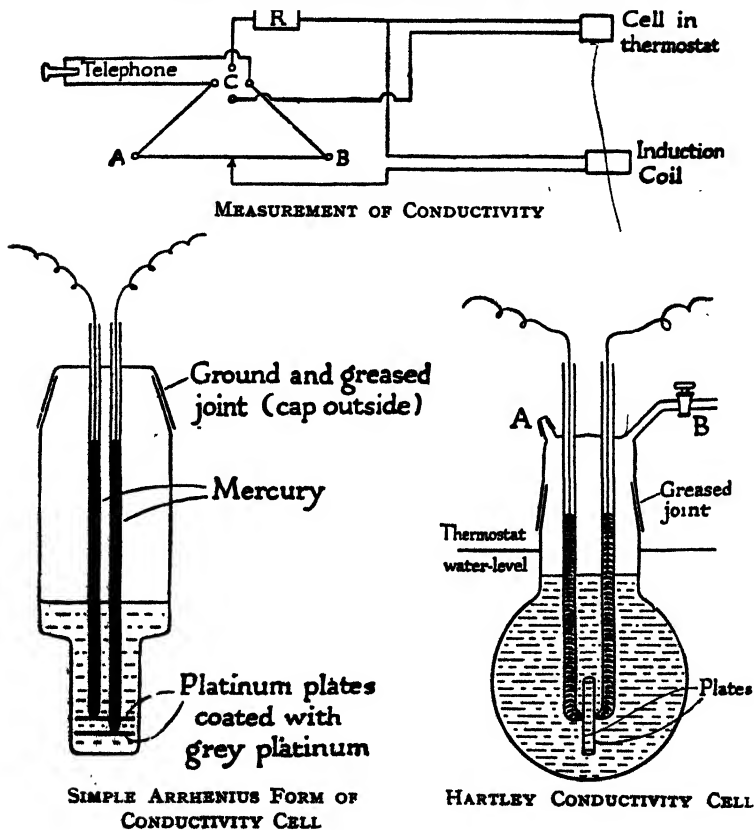
FIG. 36

induction coil or buzzer, but more recently a valve oscillator has been preferred. For conductivity measurements the solvent must be prepared in a state of special purity, since the carbon dioxide and ammonia that it may absorb from the atmosphere are sufficient to give it a marked conductivity. The purest water was prepared by KOHLRAUSCH and HEYDWEILLER by nineteen distillations in an evacuated platinum apparatus, and since that time many stills have been designed with the same purpose. Since water dissolves a

little free alkali from ordinary glass, a less soluble material, such as hard glass, fused silica, or block tin, must be used, and in most of the successful stills the water, after distillation from alkaline permanganate to remove organic matter, is boiled and fractionally condensed in a current of pure air. Conductivity-water must be carefully protected from atmospheric contamination.

The arrangement of the circuit is shown in the diagram (Fig. 36), together with two good types of cell. In the HARTLEY cell the pure solvent can be preserved from atmospheric contamination by blowing pure air free from carbon dioxide through B while a concentrated solution of the electrolyte is introduced through A. The plates are made of sheet platinum coated with grey platinum, and are held in place by small pieces of glass at each corner: by rotating the cap to which they are attached the electrolyte can be stirred.

The *specific conductivity* of a solution is defined as *the current which would flow between opposite faces of a centimetre cube of the solution at unit potential difference* (1 volt). Provided that polarization is prevented, solutions obey Ohm's law, hence the resistance can be found in a Wheatstone's bridge (though at very high potentials deviations from Ohm's law occur, the explanation of which is not yet understood). The specific conductivity of a solution is found by observing its resistance in the cell, and comparing it with the resistance of a solution of known specific conductivity, usually a standard solution of potassium chloride, in the same cell. This is both easier and more accurate than the measurement of the dimensions of the platinum plates and of the distance between them. Since conductivity is much affected by temperature, the cell must be kept in a thermostat. In a separate experiment the specific conductivity of the solvent is measured and subtracted from that of the solution; this gives the specific conductivity due to the electrolyte alone. The results are more significant if we divide the specific conductivity by the concentration, in gram-molecules per c.c., to give the *molecular conductivity*, or in gram-equivalents per c.c. to give the *equivalent conductivity*. For 'univalent' electrolytes the results are identical. The molecular conductivity is proportional to the current carried under unit potential gradient (1 volt per cm.) by the ions into which the molecule has dissociated. It represents, in fact, the average current carried under these conditions by the products of the dissociation of each molecule, and consequently varies with the concentration of the solution. At the moment we shall do no more than observe that the molecular conductivity increases as the solution becomes more dilute and reaches a maximum at what is called 'infinite' dilution, though a large class of electrolytes

is not sufficiently dissociated to approach this condition in any solution on which measurements can be made.

The Law of Independent Mobility of Ions.—The equivalent conductivity at infinite dilution cannot be directly measured and must be determined by extrapolation of results from solutions as dilute as possible. The investigation was carried out by KOHLRAUSCH in a series of researches whose accuracy, in spite of later improvements in technique, compares favourably with that of much modern research. His work was the foundation of the theory of conductivity and resulted in the important generalization known as the *Law of Independent Mobility of Ions*. He found that the equivalent conductivity of an electrolyte at infinite dilution was the sum of terms due to each ionic species, the term for each ion being a constant in all its solutions. The meaning of this observation can be explained by an example. Kohlrausch's value for the equivalent conductivity of potassium chloride at 18° and infinite dilution was 129·1. If we represent the parts of this conductivity due to the potassium and chloride ions by $\mu_K\cdot$ and μ_{Cl}' respectively, we have, if the law is true:

$$\mu_K\cdot + \mu_{Cl}' = 129\cdot1 \qquad\qquad (1)$$

Similarly the value for sodium chloride is 108·1, so that with the same notation:

$$\mu_{Na}\cdot + \mu_{Cl}' = 108\cdot1 \qquad\qquad (2)$$

For sodium nitrate:

$$\mu_{Na}\cdot + \mu_{NO_3}' = 104\cdot6 \qquad\qquad (3)$$

Assuming the law to be true, we are now in a position to calculate the equivalent conductivity of potassium nitrate from these data, and to compare our result with experiment. The value should be:

$$\mu_K\cdot + \mu_{NO_3}'$$

but from (2) and (3):

$$\mu_{NO_3}' = \mu_{Cl}' - 3\cdot5$$

so that:

$$\mu_K\cdot + \mu_{NO_3}' = \mu_K\cdot + \mu_{Cl}' - 3\cdot5 = 129\cdot1 - 3\cdot5 = 125\cdot6.$$

The value found by experiment is 125·5, and no authentic case has been produced of an exception to the law, which has been verified in both aqueous and non-aqueous solutions.

The current carried by an ion depends on two things only, viz., on the *charge* and on the *speed* with which it moves through the solution. It is obvious that ions carrying, say, a unit electronic charge will deliver twice as great a charge at the electrode in unit time if they move twice as fast as other similar ions, and hence will carry twice the current. Kohlrausch's equivalent conductivity at infinite dilution does in fact represent the sum of quantities

proportional to the speeds of the ions.   Later on we shall show how these speeds can be measured, and shall discuss the interesting conclusions to which the results seem to point.

Ostwald's Dilution Law.—Arrhenius believed that all electrolytes, except in the hypothetical condition of infinite dilution, were incompletely dissociated, and he pointed out that their degree of dissociation should be calculable at any concentraion by measuring the ratio of the equivalent conductivity at this concentration to the equivalent conductivity at infinite dilution.   The degree of dissociation a represents the fraction of the molecules of the solute dissociated at any concentration.   At infinite dilution the equivalent conductivity of an electrolyte such as acetic acid will be $\mu_{H^{\cdot}} + \mu_{Ac}'$, but if at a given dilution only a fraction a of the acid is dissociated into hydrogen ions and acetate ions, then the equivalent conductivity at this dilution will be $a(\mu_{H^{\cdot}} + \mu_{Ac}')$.   Calling the equivalent conductivity at infinite dilution and at a dilution V, Λ_{∞} and Λ_v, we have that:

$$\Lambda_{\infty} = \mu_{H^{\cdot}} + \mu_{Ac}' \quad \text{and:}$$
$$\Lambda_v = a(\mu_{H^{\cdot}} + \mu_{Ac}')$$

or:
$$a = \frac{\Lambda_v}{\Lambda_{\infty}} \qquad (4)$$

and it is from this equation that the apparent degree of dissociation can best be calculated.

Ostwald pointed out that the dissociation of an electrolyte into ions was an equilibrium that should be subject to the law of mass-action.   Thus the dissociation of acetic acid:
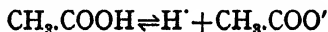
$$CH_3.COOH \rightleftharpoons H^{\cdot} + CH_3.COO'$$

ought to obey the equation:

$$\frac{[CH_3.COO'] \, [H^{\cdot}]}{[CH_3.COOH]} = K,$$

where the square brackets denote equivalent concentrations and K is a constant.   If the dilution is V, that is, if one gram-molecule of acetic acid is dissolved in V litres of water, and the degree of dissociation at this concentration is a, then $[CH_3.COO'] = [H^{\cdot}]$ $= \frac{a}{V}$, and $[CH_3.COOH] = \frac{1-a}{V}$, so that:

$$\frac{\frac{a}{V} \cdot \frac{a}{V}}{\frac{1-a}{V}} = K \text{ or } \frac{a^2}{(1-a)V} = K. \qquad (5)$$

This equation is known as OSTWALD's *Dilution Law*.   It shows how the degree of dissociation a varies with the concentration, and was tested by Ostwald for 250 organic acids in water and by BREDIG for fifty weak bases.   The application of the law to these substances was entirely successful, and each of them gave a value for K constant within the error of the conductivity determinations from which a was calculated from equation (4).   Thus, for acetic acid K was found to be about 1.8×10^{-5} at $18°$.   This means that in tenth-normal solution ($V = 10$) only about one molecule in seventy is dissociated, while in one-hundred-thousandth normal solution (which is near the limit of dilution for conductivity work) the dissociation reaches 95 per cent. K is called the dissociation-constant of the electrolyte, and its value has a very great influence on the chemical properties of the substance.

	Acids			*Bases*	
Acetic acid .	.	2×10^{-5}	Hydrazine .		3×10^{-6}
Hydrocyanic acid .		7×10^{-10}	Methylamine		5×10^{-4}
Citric acid .	.	8×10^{-4}	Aniline	.	5×10^{-10}
Benzoic acid .		7×10^{-5}			
Phenol	.	1×10^{-10}			

DISSOCIATION-CONSTANTS OF SOME WEAK ACIDS AND BASES AT $18°$

The following will serve as an example of calculations based on these figures.   EXAMPLE: At a dilution of 50 the equivalent conductivity of a certain weak monobasic acid is 9.23, while at infinite dilution its equivalent conductivity, calculated from the mobilities of the constituent ions (p. 153), is 387.   Calculate: (i) The degree of dissociation at this dilution.   (ii) The dissociation-constant of the acid.   (iii) The concentration of hydrogen ions in the solution.

(i) Call the acid HA, and let its dissociation-constant be K. Then with the previous notation:

$$a = \frac{\Lambda_v}{\Lambda_\infty} = \frac{9.23}{387} = 0.0238, \text{ or } 2.38 \text{ per cent.}$$

(ii) The concentration of undissociated acid, in gram-molecules per litre, is $(100 - 2.38) = 97.62$ per cent of $\frac{1}{50} = 0.01952$.   Hence:

$$K = \frac{[H'] [A']}{[HA]} = \frac{\left(\frac{.0238}{50}\right)^2}{.01952} = 1.16 \times 10^{-5}.$$

(iii) The concentration of hydrogen ions, as above, is:

$$\frac{.0238}{50} = 4.8 \times 10^{-4}.$$

The Anomaly of Strong Electrolytes.—The triumphant success of the Ostwald dilution law, as applied to the conductivity of weak acids and bases in water, left no doubt that the dissociation theory as originally propounded contained at least an element of truth. It was, however, obvious from the first that the dilution law broke down completely when applied to strong electrolytes, that is, to all salts and to strong acids and bases. These were proved by Kohlrausch to follow, in dilute solutions at least, the equation:

$$\Lambda_v = \Lambda_\infty - k.C^{\frac{1}{2}},$$

where k is constant for the electrolyte and C is the equivalent concentration. Λ_∞ is found by carrying the measurements to the highest practicable dilution and then plotting Λ against $C^{\frac{1}{2}}$: a straight line is obtained which when produced backwards cuts the conductivity axis at Λ_∞ (Fig. 40, p. 156). This implies a much less rapid decrease in the equivalent conductivity with rising concentration than is provided for by the dilution law, so that even at concentrations of N/10 strong electrolytes will be exerting a considerable fraction—say 70 per cent upwards—of their maximum conducting power. The values of the degree of dissociation, a, obtained by dividing Λ_v by Λ_∞, do not even approximately obey the law of mass-action, but are generally in approximate agreement with the values obtained by freezing-point measurements. It has already been pointed out that it was the anomalous molecular weights of strong electrolytes as determined by the freezing-point method that led Arrhenius to the enunciation of his theory. The anomaly is due to the dissociation of the solute, and by comparison of the true and apparent molecular weights the degree of dissociation can easily be determined. Before Ostwald's work the agreement between the values of a determined by the conductivity and freezing-point methods was Arrhenius's strongest argument for the validity of his theory, but for many years the difficulty remained —it was called the anomaly of strong electrolytes—that the mass-action law was obeyed only by electrolytes whose dissociation was very slight, that is, by the weak acids and bases.

The Complete Dissociation Theory.—In 1902 SUTHERLAND took the first step towards the solution of the problem, though for many years his views did not obtain anything like general currency. He pointed out that it was reasonable to suppose that the ionic charges, which exert forces very powerful in comparison with the gravitational forces, were not without effect on the properties of the solution. He suggested that strong electrolytes were *completely dissociated at all concentrations*, and that the change in equivalent conductivity with concentration was due to the variation in the mean distance between the ions and its effect upon the forces

between them.   In 1912 MILNER showed that this view was in quantitative agreement with the results of freezing-point measurements, and evidence was slowly collected from other branches of physical chemistry.   In 1923 DEBYE and HÜCKEL published a mathematical analysis of the problem as interpreted by conductivity measurements, and more recently ONSAGER has effected a further advance by taking into consideration the thermal agitation of the ions.

Debye and Hückel's Theory.—In these calculations two modifications are imposed upon the velocity of a particle of known dimensions moving under a given potential gradient through a medium of known viscosity, viz. (1) The arrangement of ions in a solution resembles to a slight extent that in a crystal, in that electrostatic forces cause every ion to be surrounded by a slight preponderance of ions of opposite sign.   Since the ions are in motion this causes an excess opposite charge to linger in their rear, and so retards them.   (2) The stream of ions moving in an opposite direction has a retarding effect.   Calculations on this basis lead to Kohlrausch's relation, $\Lambda_v = \Lambda_\infty - k.C^{\frac{1}{2}}$, for very dilute solutions, and from the value of k the ionic radii can be deduced.   This is, up to the present, the most successful attempt to account for the conductivity of strong electrolytes; it succeeds in aqueous solutions and is in good agreement with the results of investigations on many non-aqueous solutions.   Corrections of this kind are scarcely necessary for weak electrolytes, in solutions of which the ionic concentrations are too small for the interionic forces to be of much importance.

Transport Numbers.—We have seen that ionic mobilities are proportional to the currents carried by ions under the same potential gradient.   The fraction of the total current which each ionic species carries is called its *transport number* (symbol T).   Thus in potassium chloride the transport number of the potassium ion is $\dfrac{\mu_{K^{\cdot}}}{\mu_{K^{\cdot}} + \mu_{Cl}'} = T_{K^{\cdot}}$, and that of the chlorine ion $\dfrac{\mu_{Cl}'}{\mu_{K^{\cdot}} + \mu_{Cl}'} = T_{Cl}'$.   The equivalent conductivity at infinite dilution of potassium chloride is $\mu_{K^{\cdot}} + \mu_{Cl}'$, so that if the transport number of one ion in one solution is known, the rest can be calculated from conductivity measurements.   Apart from conductivity three methods are available:

1. The *Hittorf* method.
2. The *moving boundary* method.
3. The *electromotive force* method (p. 255).

1. In the so-called HITTORF method, in which the change in concentration round the electrodes brought about by electrolysis is measured, the solution is confined in an apparatus designed to

prevent mixing of the electrode liquids with each other or with the intervening solution. It usually consists of an H-tube: in the design illustrated (Fig. 37), which is one of the best, the central limb is bent down into a U and provided with a tap so that the middle liquid can be run out when the electrolysis is over. In these experiments only weak currents may be used, or the heat developed will lead to convection and mixing; thus the experiments may last several hours.

Let us suppose that the transport number T_{Ag^+} of silver ion in a solution of silver nitrate is to be determined, i.e. the fraction

$$\frac{\mu_{Ag^+}}{\mu_{Ag^+} + \mu_{NO_3^-}},$$ The electrodes will

be made of silver, and during the passage of a reasonably small quantity of electricity the composition of the intermediate liquid will be unaffected, since as much silver ion enters at one end as leaves at the other. If we consider a plane in the liquid perpendicular to the direction of motion

FIG. 37. MODIFIED HITTORF
APPARATUS

of the ions, the numbers of each passing it (in opposite directions) in unit time will be proportional to the speeds under the prevailing potential gradient, that is, to the fractions T_{Ag^+} and $T_{NO_3^-}$, which represent the number of gram-ions of each traversing the plane while a charge passes sufficient to deposit one gram-atom of silver on the cathode and to dissolve one gram-atom from the anode. The silver content of the liquid surrounding the cathode has therefore been reduced by one gram-atom (deposited) and increased by T_{Ag^+} gram-atoms from the middle liquid—a net decrease of $T_{NO_3^-}$. The anode liquid has gained an equal weight of silver, while the composition of the middle liquid is unchanged.

The experiment is carried out as follows. The apparatus is filled with a solution of silver nitrate of accurately known concentration and connected in series with a silver voltameter, consisting of a weighed silver cathode in silver nitrate solution. A weak current is then passed for a considerable time, and the weight of silver deposited on the cathodes is determined by weighing the cathode

F

of the voltameter. The cathode, anode, and middle solutions are run out and the first two are weighed; the silver concentration of all three is then determined. If the silver concentration of the middle liquid has remained unchanged, as it should have done, the total quantities of silver in the anode and cathode liquids, as withdrawn, are calculated, and compared with the quantities which these weights of solution contained before the experiment. The differences are converted to gram-equivalents and divided by the number of faradays which have passed through the circuit. They are then equal to each other and to T_{NO_3}', from which this fraction, which is the transport number of the nitrate ion in silver nitrate at the dilution used, can be calculated. The transport number of the silver ion is obtained by subtracting that of the nitrate ion from unity.

FIG. 38. SIR OLIVER LODGE'S EXPERIMENT IN IONIC MIGRATION

2. *Ionic mobilities* are usually expressed in the units obtained by multiplying the transport number by the equivalent conductivity at infinite dilution. The absolute velocity under unit potential gradient (1 volt per cm.) is obtained by dividing by the number of coulombs in a faraday (96,490), the result being for the potassium ion only 6.7×10^{-4} cm. per second, or about 2·4 cm. per hour. Several ingenious methods have been devised for the direct measurement of these velocities—the oldest and most striking by SIR OLIVER LODGE in 1886. He filled a long tube with a solution of common salt set with gelatine and containing phenolphthalein reddened by a trace of caustic alkali. This tube was inverted so that both ends dipped in dilute sulphuric acid connected to a battery. On passing the current the hydrogen ions moved slowly along the tube from positive to negative, thereby decolorizing the indicator; and by measuring the velocity of the boundary the ionic velocity could be calculated. If one of the ions is coloured, the indicator can be dispensed with, and it was later found that the boundary between colourless ions could be observed by the change in the refractive index of the solution at this point. For more accurate measurements some such apparatus as that shown in the diagram is suitable (Fig. 39). The narrow tube must be of uniform and known bore. To prevent mixing of the

solutions when the apparatus is filled, one of them may be fixed in position with a little gelatine, which is found not to affect the results. Let the equivalent concentrations of the salts AX and BX meeting at the boundary be respectively C_A and C_B. Suppose the upward moving boundary sweeps out a volume V c.c. during the passage of a quantity of electricity it coulombs in t seconds. B˙ in V c.c. must then have been entirely replaced by A˙. Hence $i_{A˙} \cdot t = FC_A V$, and $i_{B˙} \cdot t = FC_B \cdot V$.

Therefore $\dfrac{i_{A˙}}{i} = T_{A˙} = \dfrac{FC_A V}{it}$

and $\dfrac{i_{B˙}}{i} = T_{B˙} = \dfrac{FC_B V}{it}$

For the preservation of a stable boundary the condition is obviously $T_{A˙} \cdot C_B = T_{B˙} \cdot C_A$. The results are in good agreement with those of the Hittorf method when certain corrections have been made, particularly a correction for the water transported simultaneously with the ions. That water is so carried was proved by the American chemist WASHBURN, who arranged transport-number experiments in which a non-electrolyte such as sugar was dissolved in the liquid in addition to the salt on which the measurements were being made. It was found that at the end of the experiments the sugar concentration

Boundary

FIG. 39. DIRECT DETERMINATION OF IONIC VELOCITIES
(AX on left, BX on right)

in grams per litre was greater near one electrode than near the other, the sugar solution having been diluted at one electrode and concentrated at the other. A further method of measuring transport numbers is described in p. 255.

Ionic Mobilities.—A selection of ionic mobilities in water at 18° is given below:

Li˙	.	33·0	F′	. . .	45·8
Na˙	.	43·2	Cl′	. . .	65·2
K˙	.	64·3	Br′	. . .	67·3
Rb˙	.	66·8	I′	. . .	66·25
Cs˙	.	66·8	OH′	. . .	173·8
H˙ (H₃O)+		315·2	NO₃′	. . .	61·6
NH₄˙	. .	64·3	ClO₄′	. . .	54·9

The most striking feature of the list is the high velocity of the hydrogen and hydroxyl ions, especially the former. We must first notice that what we usually call hydrogen ion (in aqueous solution) is not actually a simple proton H^+, but the compound ion $(H_3O)^+$. The feeble but definite ionization of water thus consists in the transference of a proton from one water molecule to another contiguous to it:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-.$$

It would be correct, at least where aqueous solutions are concerned, to substitute 'hydroxonium ion' for 'hydrogen ion,' but the longer word has not found favour, and we shall continue to use the conventional description. The diameters of hydrogen ion H_3O^+ and ammonium ion NH_4^+ should therefore be comparable, and the diameter of hydroxyl ion OH^- be comparable with that of fluoride ion F^-. Since the high mobility is not attributable to small size it is probable that some special mechanism of transport of electric charge operates in aqueous solutions for the ions of water. The nature of this mechanism is still speculative, but it has recently been shown that if a proton were imagined to jump from one water molecule to the next, expelling another proton forward, this substitutional mode of transport would give a mobility much greater than that expected by a normal or direct transport. This theory does not contemplate that such a method of transport would act for ions other than those of water, so that the general revival of the discarded hypothesis of Grotthus is not probable.

The Hydration of Ions.—It has long seemed probable that ions are more or less firmly enveloped in water molecules when in aqueous solution, but the extremely divergent values emerging from different attempts to measure ionic hydration, and the new views on the constitution of liquid water (p. 103), suggest that this subject is far more complex than was formerly thought, and at present no quantitative treatment can safely be given.

Attention may however be called to the rule put forward many years ago by WALDEN, that the product of mobility into the viscosity of the solvent is approximately constant for numerous solvents, and a given ion. As the viscosity here introduced is the ordinary liquid viscosity, that is the friction of one layer of the liquid against another, the validity of this rule seems to indicate a 'solvation' of ions. As the result of X-ray analysis more definite conclusions have been reached about the hydration of ions in crystals, and on the constitution of hydrated crystals generally. The structure of nickel sulphate $NiSO_4.7H_2O$ has been very fully worked out, and there is little doubt that the results are applicable in general to all the so-called 'vitriols' of formula $M.SO_4.7H_2O$

(M=Mg, Zn, Ni, Co, Fe, etc.). The features of the structure are broadly indicated by writing the formula as

$$[(Ni.6H_2O)^{++}.SO_4{}^{--}]H_2O.$$
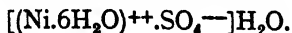
Six molecules of water closely surround the cation octahedrally, while the remaining molecule plays a more general part in stabilizing the structure as a whole. The close association of some or all of the crystal water with the cation is also found in $(Be.4H_2O)SO_4$ $[(Cu.4H_2O).SO_4]H_2O$, $(Mg.6H_2O)Cl_2$, and $(Al.6H_2O)Cl_3$. The tendency in crystals for the cation to be hydrated rather than the anion is in harmony with the fact that in general free cations, especially when multiply-charged, are smaller than anions (see p. 93). The intense electric field at the surface of small cations initiates the binding of water molecules firmly, and the sizes of the hydrated cations become comparable with those of the anions. The prevalence of the typical ' co-ordination numbers ' four and six probably indicates a definite chemical interaction between the cation and its hydration water (see p. 345). While it is possible that such a distinction between cations and anions operates in solution, the position therein must be greatly complicated by the competing structure of water itself. A given ion can relegate water to itself only if the hydrate formed is more stable than the water structure destroyed in its formation.

Results of Conductivity Work in Water.—Before we close our discussion of the work on which the dissociation theory is based we shall have to refer shortly to non-aqueous solutions, and it may be well at this point briefly to summarize the essential results of conductivity work in water. We have seen that the only satisfactory explanation of Faraday's laws is that the current is carried in equal units by ions produced from the solute by dissociation, and that in weak electrolytes, a class which in water consists only of weak acids and bases, the degree of dissociation is comparatively small and can be calculated from the ratio of the equivalent conductivity to the maximum value which it reaches at infinite dilution. Ordinary concentrations so little resemble this condition that the equivalent conductivity at infinite dilution cannot, as with strong electrolytes, be obtained directly by extrapolation of the curve connecting it with the concentration (or, better, with its square root), but must be indirectly calculated as the sum of the mobilities of the ions at infinite dilution, which may themselves be calculated from the data of strong electrolytes. Thus the mobility of the acetate ion, and hence the conductivity of acetic acid at infinite dilution, must be obtained by measuring the equivalent conductivity at infinite dilution of the strong electrolyte sodium acetate and subtracting from it the mobility

of the sodium ion. The degree of dissociation calculated in this way for weak electrolytes shows that their dissociation obeys the law of mass-action, a conclusion embodied in Ostwald's dilution law. To bring out the difference between strong and weak electrolytes the diagram (Fig. 40) shows the equivalent conductivity at 18° of hydrogen chloride and hydrogen acetate solutions at high dilution (infinite dilution to N/200) plotted against the square root of the concentration.
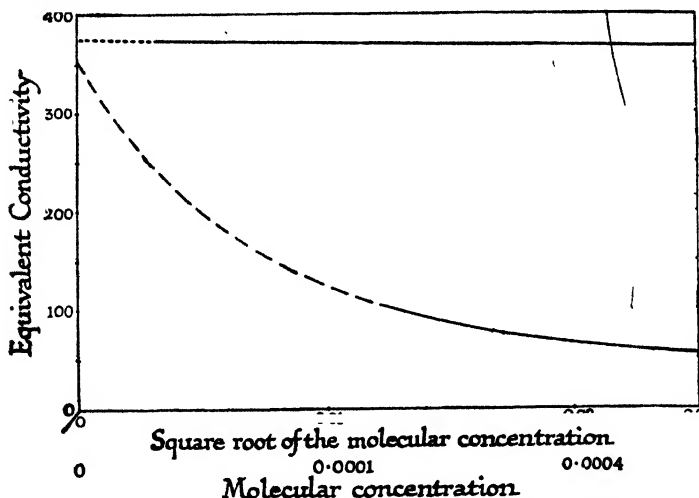
FIG. 40. EQUIVALENT CONDUCTIVITY OF A STRONG AND A WEAK ELECTROLYTE
(Hydrochloric acid above, acetic acid below)

Strong electrolytes comprise strong acids and bases and nearly all salts, including the salts of weak acids and bases. They do not obey Ostwald's dilution law, and their equivalent conductivity in dilute solution is a linear function of the square root of the concentration. They are highly dissociated at all concentrations, and modern work appears to indicate that this dissociation is in fact complete, and that the decrease in equivalent conductivity with concentration is due to the electrical forces between the ions. Kohlrausch's law of the independent mobility of ions is shown to be a logical consequence of the dissociation theory, and with the help of transport-number experiments it is possible to calculate the absolute velocity of an ion under a given potential gradient. The mobilities calculated from these data are not in agreement with estimates of atomic volume, a discrepancy explainable by the conception that many ions carry with them several molecules of water of hydration which must be included in the ionic radius.

The Activity Concept.—Since the dissociation of strong electrolytes does not obey the law of mass-action, which has been of so great assistance in examining equilibria of other·types in solution, efforts have been made to develop other relations to take its place. The *activity* of an ion or molecule represents the function that must be substituted for its concentration if the law of mass-action is to be rigidly obeyed. It is usually not proportional to the concentration. The activity divided by the concentration is called the *activity coefficient.*

Since perfect gases rigidly obey the law of mass-action, their activity-coefficients are always unity. Most gases are nearly perfect in their behaviour at moderate pressures, and the activity of a volatile solute, e.g. hydrogen chloride, in two solutions of different concentration can therefore be compared by determining the ratio of its partial pressures over the two solutions. To determine the activity at any one concentration, an arbitrary value must be given to the activity or activity-coefficient of the substance at some fixed concentration. A method of determining activity coefficients for the ions of electrolytes is described in Chapter VIII, p. 252.

Non-aqueous Solutions.—Further information on many difficult matters in connection with solutions would be desirable, and this we might expect to gain from an examination of solutions in solvents other than water. A great deal of work has been done, chiefly in solvents of moderately high dielectric constant, in which, as has already been pointed out, dissolved substances are more highly dissociated than in solvents of low dielectric constant, which, indeed, have often little or no power of dissolving electrolytes. Unfortunately the properties, and especially the conductivity, of non-aqueous solutions are enormously affected by the presence of small quantities of water or other impurities, and for this reason much of the older work is of doubtful value. However, reliable work has been done in methyl and ethyl alcohol, acetone, acetic acid, liquid ammonia, nitromethane, acetonitrile and other solvents, and though the results indicate that still further research is needed, some interesting generalizations have emerged.

Results of Conductivity Work in Non-aqueous Solutions.—In non-aqueous solvents the sharp distinction between weak and strong electrolytes disappears, and the chemical nature of the ions plays a specific part in the variation of equivalent conductivity with dilution. Thus, while Kohlrausch found that in water all ordinary salts (some mercury compounds are the best-known exceptions) obeyed the square-root relation and were markedly regular in their behaviour, the same cannot be said of solutions in any one non-aqueous solvent. Among them the hydroxylic solvents, i.e. the alcohols, most closely resemble water in their

behaviour. In particular, in these solvents the hydrogen ion has a mobility much greater than that of other ions, just as it has in water. The table shows the mobility at 25° of the hydrogen ion in methyl and ethyl alcohols, two hydroxylic solvents which have been thoroughly investigated by HARTLEY and others, and in the two non-hydroxylic solvents acetone and nitromethane. The mobility of the ammonium ion is given for comparison

	Water H_2O	Methyl Alcohol $CH_3.OH$	Ethyl Alcohol $C_2H_5.OH$	Acetone $(CH_3)_2CO$	Nitromethane $CH_3.NO_2$
H·	351	142	59·5	88	63
NH₄·	74	58	19	98	64

MOBILITY OF THE HYDROGEN AND AMMONIUM IONS AT 25°

In attempting to interpret these data it must be remembered that by the 'mobility of hydrogen ion' we strictly mean only the rate of transport of unit positive ionic charge, and we can be sure that if the electric transport is effected by a simple ionic diffusion the ion concerned is never a simple proton. It is possible that the 'jumping' mechanism proposed for water also operates in hydroxylic solvents such as the alcohols, but, as might be expected, less efficiently. In ethyl alcohol the mobility is of the magnitude to be expected for the simple diffusion of an ion of the form $C_2H_5OH_2^+$. The nature of the conduction process in such solvents as acetone and nitro-methane is little understood, and the near equality of the mobilities of 'hydrogen' and ammonium ions in these solvents may be fortuitous.

Effect of the Dielectric Constant.—It has already been stated that the dielectric constant of a solvent has an important influence on its ionizing powers, the most noticeably ionizing solvents being those with high dielectric constants. The presence of a hydroxyl group in the solvent molecule has an equal if not greater effect. The diagram (Fig. 41) shows the equivalent conductivity of nitric acid and perchloric acid in various typical solvents plotted against the square root of the concentration. For the better comparison of the results, the equivalent conductivity is expressed as a fraction of the equivalent conductivity at infinite dilution. It will be noticed:

(i) That in water and the alcohols the conductivity of either acid at any concentration decreases with the dielectric constant.

(ii) That the conductivity of nitric acid is much more affected by change of solvent than is that of perchloric acid. Only in water is nitric acid a strong electrolyte.

(iii) That the influence of the hydroxyl group outweighs that of

the dielectric constant, since the conductivities are higher in ethyl alcohol (dielectric constant 25) than in nitrobenzene (dielectric constant 35).
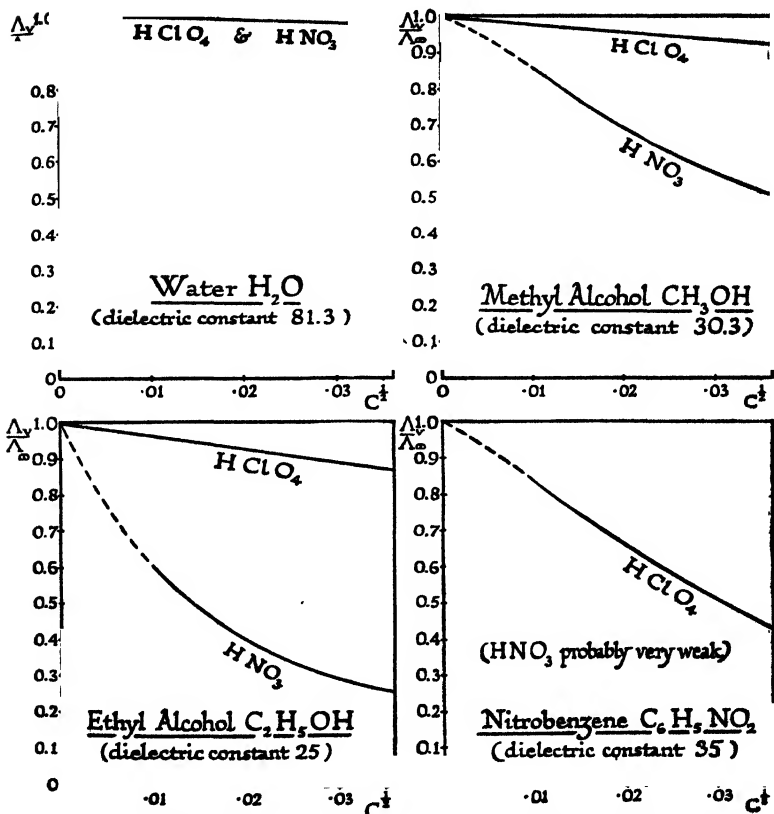
FIG. 41. PERCHLORIC AND NITRIC ACIDS IN DIFFERENT SOLVENTS

$\left(\dfrac{\Lambda_v}{\Lambda_\infty} \text{ plotted against } C^{\frac{1}{2}}\right)$. (25°)

Hydroxylic Solvents.—The high ionizing powers of hydroxylic solvents are probably connected with the polar properties of the hydroxyl group (Chapter XI), which enable it to act either as donor or acceptor, and in such solvents both cation and anion may be solvated. The process of ionization in solution consists not only in a separation of the constituents of the solute molecule:

$AB \rightarrow A^{\cdot} + B'$, but also in the combination of both of them with the solvent:

$$\text{Solvent} + AB \rightarrow (\text{Solvent.A})^{\cdot} + (\text{Solvent.B})'.$$

Many electrolytes are fully ionized only in solvents of very high dielectric constant, e.g. in water, since the conductivity curves obtained in non-aqueous solvents often oblige us to suppose that a considerable proportion of undissociated molecules is present.

Ionization and Fajans' Theory.—Among the many acids so far investigated, perchloric acid best retains its character as a strong
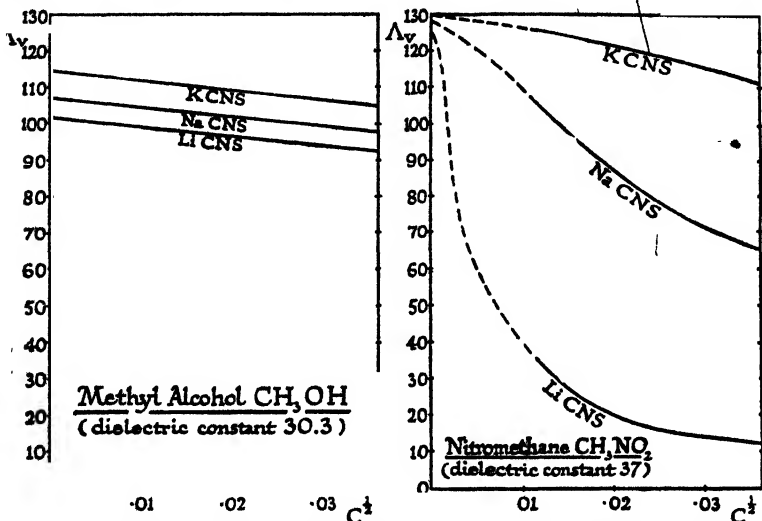
FIG. 42. CONDUCTIVITY OF THIOCYANATES IN NON-AQUEOUS SOLUTIONS (25°)

electrolyte when dissolved in non-aqueous liquids. Among salts the effects of different solvents are complicated and specific, and classes of salts which show perfect regularity in water may show great divergence in other solvents. On the whole, the tendency to ionization is what we should expect from FAJANS' theory (p. 340), that is, it is promoted by a large cation and a small anion. The thiocyanates of lithium, sodium, and potassium may be taken as an example. Fig. 42 shows their equivalent conductivities in methyl alcohol and nitromethane at 25° plotted against the square root of the concentration. In methyl alcohol, as in water, the curves are nearly parallel straight lines. In nitromethane, on the other hand, the tendency to ionization is much greater in the potassium salt, with its large cation, than in the lithium salt, with its small one. In applying

Fajans' theory to hydroxylic solvents it is usually necessary to take into account the effect of solvation.

Recent conductivity work shows then that the dissociation of electrolytes is a very much more complicated problem than was supposed when the original theory of Arrhenius was introduced. The theory of complete dissociation, again, must be restricted to dilute solutions in water and a few other solvents of high dielectric constant. Much work remains to be done on the subject.

Evidence for the Dissociation Theory.—It will be convenient at this point to give a list of some of the more important experimental facts on which the dissociation theory in its widest sense is based. It has become so much a part of chemistry that with every year it grows more difficult to distinguish between fact and theory, but it is important that such a distinction should be maintained.

1. The conductivity work discussed in this chapter, and particularly the identity of the electronic charge with that required to deposit a univalent atom from solution.

2. The distinction between electrolytes and non-electrolytes revealed by osmotic pressure and related properties (vapour pressure, freezing- and boiling-points).

3. The ionization of crystals (p. 86).

4. Calculations of dissociation-constants of weak electrolytes by several different methods give concordant results: see for instance the calculation of the ionization-constant of water (p. 191). On the other hand, strong electrolytes still present puzzling features.

5. The properties of solutions appear to be the sum of the properties of their ions—e.g. all permanganate solutions are pink; a solution of sodium nitrate and potassium chloride cannot be distinguished from a solution of sodium chloride and potassium nitrate. No properties can be ascribed to the undissociated molecules of strong electrolytes in solution, and as they are known not to exist in the solid state it seems illogical to postulate their existence in solution.

6. The heat of neutralization of strong acids and bases is constant (p. 193).

7. The dissociation theory provides a fairly close quantitative explanation of ionic equilibria such as those involved in precipitation (p. 194).

8. Distribution experiments such as those of Knight and Hinshelwood (p. 184).

9. Experiments with radioactive indicators (p. 320).

SUGGESTED FOR FURTHER READING

GLASSTONE: *Electrochemistry of Solutions* (1945).
HILDEBRAND: *Solubility*.
AUDRIETH and KLEINBERG: *Non-aqueous Solvents* (1952).

CHAPTER V

HETEROGENEOUS EQUILIBRIUM

The phase rule—Derivation of the phase rule—One-component systems—
Two-component systems—Distillation—Immiscible liquids—Solid-liquid
systems—Effect of compound-formation—Effect of mixed-crystal forma-
tion — Freezing-mixtures — The distribution law — Distribution in con-
centrated solutions—Experimental devices—Effect of the molecular
species—Combination with the solvent—Dissociation—Practical applica-
tions to association, dissociation, extraction, and other equilibria in solution.

The Phase Rule.—A homogeneous part of a heterogeneous system
is called a *phase*. Heterogeneous equilibrium is the name given to
equilibrium in systems containing matter in more than one phase.
A solid may consist of any number of phases if it is heterogeneous—
e.g. a block of granite containing embedded crystals—and the same
applies to liquids; thus two immiscible liquids in contact are con-
sidered to be two phases. But since all gases are completely
miscible, a single system cannot contain more than one vapour
phase. It is true that these premises are in contradiction to the
molecular theory, which declares all matter to consist of separate
particles, but we are justified in maintaining them so long as we
apply them only to such large numbers of molecules that statistical
laws are obeyed with precision.

The fundamental law to which all cases of heterogeneous equi-
librium must ultimately be referred is the *Phase Rule*, originally
introduced by WILLARD GIBBS (1839–1903), Professor of Physics
at Yale University. The highly abstract nature of this generaliza-
tion hinders it from giving much assistance to an elementary
student, but on account of its wide application we shall begin by
giving a general demonstration of it and apply it later to the
various cases of heterogeneous equilibrium with which we deal.

We define the number of *components* in a system as the number
of substances whose amounts we are free to fix arbitrarily when the
temperature and total volume of the system have been specified.
An example will help to make this clear. Consider a system contain-
ing hydrogen, iodine, and hydrogen iodide, in equilibrium. There are
three substances present, but only two components, because if to the
system in equilibrium we add, at constant volume, an additional
quantity of the substance we have excluded from the list of
components it will affect the amounts of the other two, that is to

say, its amount cannot be varied independently. Any two of the substances can be selected as components; when their amounts are fixed, the amount of the third substance in equilibrium with them under the same conditions is likewise fixed. Notice that while the *amounts* of the components present are of prime importance, the same is not true of the amounts of the phases, but only of their *number*. Thus so long as liquid water remains in a system containing only water and water-vapour, the vapour pressure at constant temperature is constant and is quite independent of the amount of liquid water remaining. When one of the phases reaches microscopic dimensions this is no longer true (see, for example, p. 282), but we have already excluded such systems from our treatment. We shall also exclude systems acted on by exterior forces such as gravity or electrical fields, considering only the effect of temperature, pressure, and volume.

Derivation of the Phase Rule.—Consider a system containing one phase and one component, e.g. an enclosure containing steam but nothing else. Experience shows that in such a system temperature, pressure, and volume (or its reciprocal the concentration) are interdependent. We cannot fix two of them without also fixing the third. In the example we have chosen, the concentration C, defined as the reciprocal of the volume V, is connected with the absolute temperature T and the pressure p by the relation $C = \dfrac{1}{V} = \dfrac{p}{RT}$. For any other one-phase one-component system some relation must exist between C, p, and T; let us write it $C_1 = f_1(T_1, p_1)$.

Let us now consider a system containing two phases but one component, e.g. an enclosure containing water and water-vapour. For each phase we have one equation, namely $C_1 = f_1(T_1, p_1)$ and $C_2 = f_2(T_1, p_1)$. In the example we have chosen the equation applying to the liquid phase will not be in the form $pV = RT$, but will be a much less simple relation describing the variation of the volume of unit mass of liquid water with temperature and pressure. Now there will be a constant exchange of material between the two phases. In our example, water will be continually entering the liquid phase from the vapour phase and vice versa. The rate at which water leaves the vapour phase will be a function of the temperature, pressure, and concentration in that phase; call it $f_1(T_1, p_1, C_1)$, and call the rate at which water leaves the liquid phase $f_2(T_1, p_1, C_2)$. If the system is in equilibrium, the rate at which water leaves one phase is equal to the rate at which it leaves the other, so that:

$$f_1(T_1, p_1, C_1) = f_2(T_1, p_1, C_2).$$

However numerous the components, an equation can be written connecting their concentrations in each phase with the temperature and pressure, and for each pair of phases an equation can be written for each component expressing the equality of its tendencies to pass from one to the other. Now P phases can be arranged in P—1 pairs, so that if there are n components there will be P equations of the first kind and $n(P-1)$ equations of the second kind, making a total of $P(n+1)-n$ equations. The variables in these equations are nP concentrations, temperature, and pressure (these two must be the same throughout the system at equilibrium), or nP+2 in all. We have therefore $P(n+1)-n$ equations containing nP+2 variables. In order to determine these variables $2+n-P$ more equations are required, or in other words we may assign arbitrary values to $2+n-P$ variables without violating any of the equations we have already deduced. This number $2+n-P$ is therefore said to denote the number of *degrees of freedom* of the system: the phase rule states that the number of degrees of freedom (which we may denote by F) is given by the equation $F=2+n-P$, or:

Number of Phases+Number of Degrees of Freedom $=Number of Components+2.$

Let us take an example. Ether is slightly soluble in water, but if the mixture contains more than a small proportion of ether it separates into two layers, one consisting of ether saturated with water, the other of water saturated with ether. If this proportion has been exceeded, a system containing the mixed liquids and vapour will consist of three phases—two liquid and one gaseous. Since the number of components is 2, the system should have $2+2-3=1$ degree of freedom, and if we fix, for example, the temperature, the vapour pressure must be invariable. This is found to be true. But if there is not enough ether to saturate the water there will be only two phases, one liquid and one gaseous, and the number of degrees of freedom should be $2+2-2=2$. If then the temperature is fixed we can still vary arbitrarily either the concentration of the solution (that is, the proportion of ether in it) or the pressure, but not both, and this also is true.

One-component Systems.—With one component in one phase, there are two degrees of freedom. Thus if a vapour is contained in an enclosure, we can vary either the temperature and the pressure, or the pressure and the concentration (defined as the mass of vapour in the enclosure), or the temperature and the concentration. With one component in two phases, there is one degree of freedom; thus the vapour pressure of a liquid (or a solid) at a fixed temperature is a constant, or again the melting-point of a solid at a fixed pressure (i.e. the temperature at which it is in equilibrium with liquid) is a constant.

With one component in three phases the system has no degrees of freedom, i.e. it is *invariant*. For example, the diagram (Fig. 43) shows the relations between pressure and temperature of a system containing solid, liquid, and vapour of the same substance, or any two of them. OA is the vapour-pressure curve of the solid, CC′ the vapour-pressure curve of the liquid. These curves cut at O,
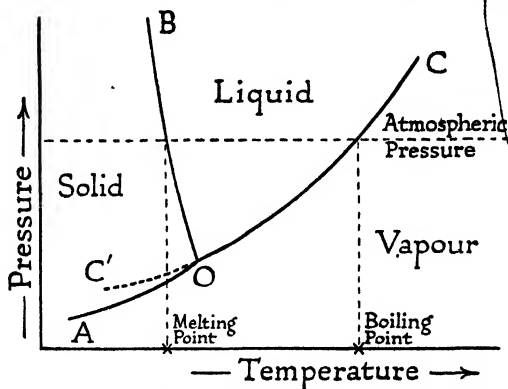
FIG. 43. A THREE-PHASE ONE-COMPONENT SYSTEM

and the abscissa of this point is the melting-point of the substance at a pressure represented by the ordinate of O. As the pressure is increased above this value a change takes place in the melting-point, which may be either raised or lowered. The connection between the pressure and the melting-point is given by OB, which in the diagram is drawn for a substance whose melting-point is reduced by increased pressure; Le Chatelier's rule tells us that it must be a substance like water that expands on freezing.

Between AO and BO the stable form is solid, between BO and CO liquid, and between CO and AO vapour. Along AO solid and vapour can exist together in equilibrium, along BO solid and liquid, along CO liquid and vapour. Only at one point, O, called the triple point, can solid, liquid, and vapour exist together in equilibrium; hence if all these phases are to be present the system is invariant. The triple point of the ice–water–water-vapour system lies at a pressure of 4·6 mm. of mercury and a temperature of +0·008° C.

It will be observed that the liquid-vapour curve has in the diagram been produced beyond the triple point to C′. This is in agreement with observation, since in the absence of the solid phase liquids can often be undercooled to temperatures far below

their freezing-point without solidification. Phases which persist under conditions in which they should normally disappear are said to be *metastable*. The vapour pressure of the metastable phase is always higher than that of the stable phase: if this were not so isothermal distillation could take place from the more stable phase to the less stable. Since the stable phase is defined as that which cannot spontaneously change, this is impossible. This has been verified for ice and water: water can be undercooled to about −10° C., as FAHRENHEIT discovered more than two hundred years ago, and the vapour pressure of water at any temperature below 0° C. is greater than that of ice at the same temperature. Solidification can always be brought about by the addition of a small fragment of the solid, and this behaviour recalls that of super-saturated solutions. Analogously water, when suspended as drops in a liquid of equal density, can be heated to about 180° without boiling: there are, however, no recorded cases of a solid being heated above its melting - point without melting. An interesting example of metastability is afforded by the allotropic modifications of tin. It has long been known that in unusually

FIG. 44.   THE VAPOUR PRESSURE OF TIN

severe cold weather articles made of tin are liable to crumble to a grey powder. This grey form of tin is an allotropic modification and is the stable form up to a temperature of 13° C. Under ordinary winter conditions white or ordinary tin is in fact metastable. The permanence of tin articles is due to the extreme slowness of the change from the metastable to the stable state. The change is promoted by cooling to temperatures considerably beneath 13°. The measurement of the vapour pressure of tin is a matter of great difficulty on account of its extremely low value, but if the vapour pressures of the two forms were plotted against the temperature, the curves would intersect at 13° as in the diagram (Fig. 44). Above 13° white tin has the lower vapour pressure and is the stabler form; below 13° its vapour pressure is higher than that of grey tin and it is metastable. It has already been pointed out that the phase rule can be applied only to systems that have reached stable equilibrium.
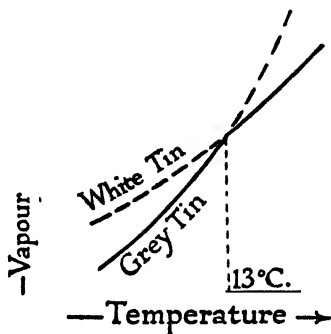
Two-component Systems.—Systems containing two components and two phases can exist in a great variety of forms. We shall

consider one or two representative cases of the systems solid-vapour, liquid-vapour, liquid-liquid and solid-liquid. In all these systems, there will be two degrees of freedom as long as the number of phases remains at two. It might be supposed that this would apply to the well-known examples of equilibrium between hydrated salts and water-vapour, but it is evident that as soon as the given hydrate either loses water or takes it up to form a lower or higher hydrate the system must be considered to contain two solid phases, making three in all, and has therefore only one degree of freedom. If the temperature is fixed the pressure of water-vapour must then remain at a fixed value. This rather surprising deduction is in agreement with experiments made long before the phase rule was understood. Thus compounds such as $CuSO_4.5H_2O$ and $CuSO_4.3H_2O$ can exist together in equilibrium only in the presence of water-vapour at a definite pressure. If the actual pressure exceeds this value, some $CuSO_4.3H_2O$ will take up water to form $CuSO_4.5H_2O$, whereas if the value is not reached, some $CuSO_4.5H_2O$ will lose water to form $CuSO_4.3H_2O$ (*efflorescence*). If only one hydrate is present the total number of phases is two and the system has two degrees of freedom, so that at constant temperature such a compound as $CuSO_4.3H_2O$ is stable between definite limits of pressure of water-vapour.

Solids that dissolve in the water they absorb from moist air are said to be *deliquescent*. A solid deliquesces if the pressure of water-vapour in the surrounding atmosphere exceeds the vapour pressure of its *saturated solution*.

Distillation.—In liquid-vapour systems relations are perhaps slightly more difficult to understand, but the practical applications are at least of equal importance, since they include the behaviour of liquids on distillation. We shall first deal with liquids miscible in all proportions, representing their relations by means of isobaric curves connecting composition and temperature. The isothermal curves connecting composition and pressure can be treated in a somewhat similar way, and the relations between composition, pressure, and temperature can all be represented simultaneously by a space-model of curved surfaces.

The diagram (Fig. 45) represents the connection between the temperature and the composition of the liquid and vapour phases of two completely miscible liquids A and B at constant pressure. The point A is the boiling-point of A at that pressure, B is the boiling-point of B. The curve AXB shows the connection between the boiling-point of the liquid and its composition. As we shall see, it can have more than one form, and may show a maximum or a minimum: the simple form shown in this diagram is usually found when the two components are closely related chemically.

MN is parallel to the composition axis. M represents the

temperature at which a liquid of composition L will begin to boil. The point Y on MN represents the composition P of the vapour in equilibrium with the liquid. The upper curve connecting A and B is made up of such points, and just as M is the temperature at which a liquid of composition L begins to boil, so is it the temperature at which a vapour of composition P begins to condense. Below AXB only liquid can exist, above AYB only vapour, between them liquid and vapour can exist together.

Suppose now that the liquid of composition L is to be distilled at constant pressure. When the temperature reaches M the liquid boils and vapour of composition Y leaves the system. This vapour is richer than the liquid is in component B (which has the lower boiling-point), and the liquid is thus left richer in component A. After a short interval its composition will be represented by L', and the boiling-point will be M'. The vapour also becomes pro-

TWO COMPLETELY MISCIBLE
LIQUIDS: PHASE DIAGRAM

gressively richer in component A, and at this point has the composition P'. If the distillation is stopped at this point, the liquid mixture has been separated into two parts: a residue of composition L', richer in A than the original mixture, and a distillate of composition somewhere between P and P', richer in B than the original mixture. By again distilling these liquids a further separation can be effected, and by uniting the middle fractions and redistilling them it is in time possible to obtain reasonable yields of liquids closely approximating to pure A and pure B in composition. It is, however, impossible by a finite number of distillations to obtain finite quantities of either pure A or pure B. The efficiency of the process can be improved by the use of a long fractionating column, in which the ascending vapour is brought into equilibrium with the condensed liquid.

If the boiling-point curves show minima or maxima (Fig. 46) the conditions are still less favourable for separation. Water and ethyl alcohol are an example of the first, water and nitric acid

of the second. At the minimum or maximum the liquid and vapour phases in equilibrium are of identical percentage composition, so that a liquid with this composition is unchanged by distillation. Such liquids are called *constant boiling mixtures*. After a mixture of water and ethyl alcohol has undergone a large number of fractionations the resulting liquids will approximate in composition to the constant-boiling mixture and one or other of the
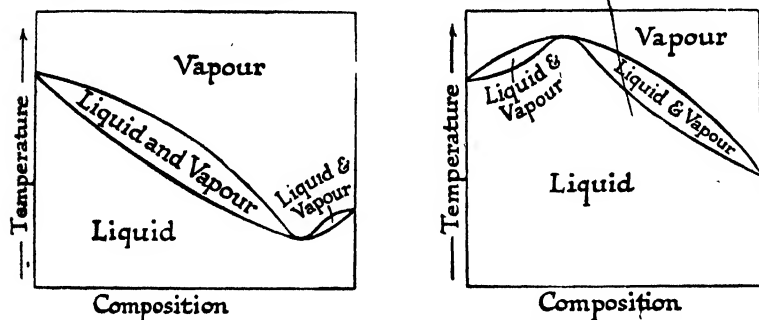
FIG. 46. VAPOUR PRESSURE OF TWO COMPLETELY MISCIBLE LIQUIDS

components: water if the original liquid contained more water than the constant-boiling mixture, and ethyl alcohol if it contained less. Water and hydrogen chloride also form a constant-boiling mixture which contains about 20 per cent hydrogen chloride at 760 mm.; the preparation of this solution by distillation is one of the most accurate methods of obtaining a standard solution of the acid for volumetric analysis. It is merely necessary to distil the 20 per cent acid (density very nearly 1·1 gm. per c.c. at 15°) at the rate of 3 to 4 c.c. a minute, rejecting the first three-quarters of the distillate and leaving some residue in the flask. The remainder of the distillate then contains exactly 20·221 per cent of hydrogen chloride by weight, if the barometer stands at 760 mm.; for other barometric readings a very small correction is required.

Immiscible Liquids.—In systems containing two liquid components we shall for the moment consider only the two liquid phases that exist when the liquids are not completely miscible. In the absence of the vapour phase the system has two degrees of freedom, so that if the temperature and pressure are fixed there is only one possible value for the composition of each phase. The system then consists of a saturated solution of A in B and a saturated solution of B in A. In Figs. 47 and 48 the points X and Y represent the compositions of saturated solutions of B in A and of A in B, both at a temperature T_1. If the solubilities increase with temperature,

as in Fig. 47, or decrease, as in Fig. 48, the curves must meet to form a maximum or minimum respectively, at a temperature called the *critical solution temperature.* Inside the curve two liquid layers exist in equilibrium, outside it only one; it is therefore impossible for two layers to separate out above this temperature (in case 1) or below it (in case 2). Organic compounds are known with which water form mixtures of both types, and pairs of liquids have also been discovered whose solubility curves are closed at both ends. The behaviour of water and aniline is of the type shown in Fig. 47. Fig. 48 shows the type of behaviour of water and dimethylamine, and water and nicotine give a closed curve.

A system containing two immiscible liquids and a vapour phase has only one degree of freedom, and the vapour pressure at a fixed temperature is independent of the composition (Fig. 49), being equal to the sum of the vapour pressures of the components. Since all liquids have some mutual solubility, however small, this type of relation is no more than a limiting case, though such pairs of liquids as water and mercury approach it very closely. When the liquids are partially miscible the most usual type of curve is that shown in Fig. 50; the vapour pressure, in accordance

Fig. 47

Fig. 48

Figs. 47 & 48. Mutual Solubility of Two Liquids

with the phase rule, is constant only over that part of the range (BC in the diagram) within which two liquid phases are stable. Ether and water form a system of this type.

Liquids with high boiling-points, if they are immiscible with water, can frequently be separated from impurities by steam distillation at about 100°, an operation common in organic chemistry. Avogadro's principle and the gas laws show that the numbers of molecules of the organic liquid and of water in the distillate are proportional to the vapour pressures of the liquid and of water at this temperature, and from this relation the proportion by weight can be calculated if the vapour pressure and molecular weight of

the liquid are known.   The only function of the steam is to accelerate the vaporization of the liquid to be distilled by sweeping its vapour from the distillation flask.   Water itself can be removed by distillation below 100° with an inert liquid (see hydrogen peroxide, p. 379). The advantage of these processes is the low temperature at which distillation can be carried out.
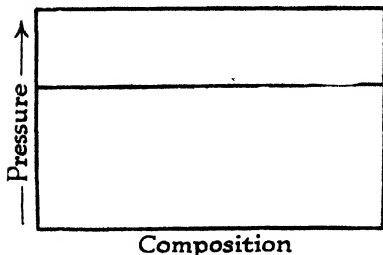
FIG. 49
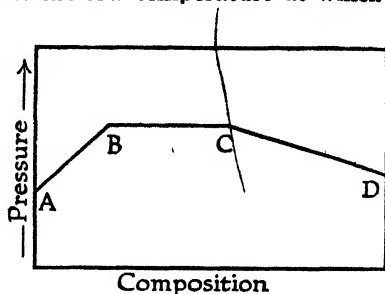
FIG. 50

VAPOUR PRESSURE OF IMMISCIBLE AND PARTIALLY IMMISCIBLE LIQUIDS

Solid-liquid Systems.—Solid-liquid systems are, from the industrial standpoint, perhaps the most important of all those to which the phase rule can usefully be applied.   Some such guide is essential in investigating the preparation and properties of alloys.   For a full description of these systems a textbook of metallurgy must be consulted; we shall restrict ourselves to the more important types of two-component systems generally containing only two phases.

It will be necessary at the outset to decide how many phases are to be assigned to the solid mixture containing both components. Homogeneity must be the criterion—heterogeneous mixtures contain two or more phases, homogeneous only one.   Homogeneous two-component solids are called either 'mixed crystals' or 'solid solutions,' and they are detected either by examination of a section under the microscope or by the peculiar form which they give to the phase diagram.

Since the melting-points of solids are only slightly affected by changes of pressure, the most informative diagrams for solid-liquid systems are those connecting temperature and composition.   Fig. 51 shows the relations at constant pressure between two components which form neither a compound nor mixed crystals.   The component A melts at a temperature represented by A, while B melts at B.   The addition of B to A lowers the freezing-point of A, and the curve AC (which with BC is called the *liquidus*) shows the freezing-points of such mixtures.   Similarly the lowering of the freezing-point of B brought about by the addition of A is repre-

sented by BC. These curves meet at C (called the *eutectic point*). Since at C the two solid phases A and B can coexist in equilibrium with the liquid phase, the system has only one degree of freedom. It follows that if, as in this case, the pressure is fixed, the position of the eutectic point is fixed both as regards temperature and composition.

Liquids of any other, than the eutectic composition deposit either pure A or pure B on freezing, according as they contain more or less of these components than the eutectic mixture contains.
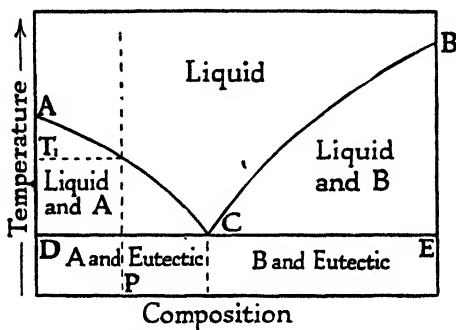
FIG. 51. TWO IMMISCIBLE SOLIDS: PHASE DIAGRAM

If, for example, the liquid of composition P be cooled, it will at a temperature T_1 deposit pure solid A.   This leaves the liquid richer in B, and the temperature gradually sinks as the composition changes in a way represented by the curve AC.   At C the whole of the remaining liquid, which now has the eutectic composition, solidifies.   If a solid mixture, containing let us say more component B than corresponds with the eutectic composition, is heated, it begins to melt as soon as the eutectic temperature is reached, and the liquid formed has the eutectic composition.   This leaves the solid richer in B, and its composition-temperature relations are represented by CE until all the component A is present in the liquid phase.   The melting-point then rises sharply as the component B melts, until the system is wholly liquid at a temperature located on the line CB.

The course of the liquidus is usually determined by means of a series of cooling curves on different mixtures.   In such an experiment the liquid is contained in a vessel in an enclosure free from draughts and at a temperature well below the eutectic temperature.

Readings are taken at equal intervals of time with a thermo-
meter or thermocouple in the liquid. To ensure equilibrium it
must be kept well stirred. The rate of loss of heat from the
vessel depends only on the difference in temperature between the
vessel and its surroundings, so that if any change takes place in
the liquid in which heat is absorbed or liberated it will betray
itself by a change in the rate of fall of temperature. The diagram
(Fig. 52) shows such a plot of time against temperature. T_1 is the
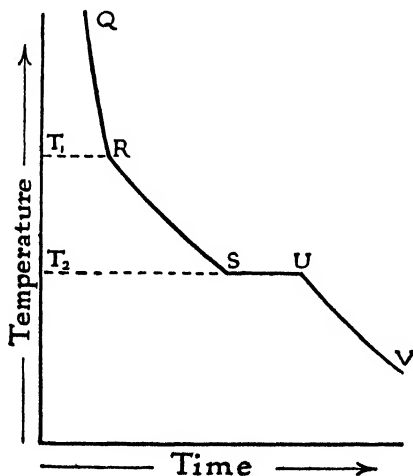
FIG. 52. COOLING CURVE OF A BINARY MIXTURE

freezing-point on the liquidus; at this point one of the pure com-
ponents begins to separate. The loss of heat from the containing
vessel is now partly supplied by the latent heat of fusion, and the rate
of fall of temperature is thereby diminished, hence at R the slope of
the curve suffers an abrupt change. T_2 is the eutectic temperature.
At this point the whole of the remaining liquid has the eutectic
composition, and solidifies at a rate exactly sufficient to provide
enough latent heat of fusion to balance the loss of heat by cooling,
for when both the liquid and solid forms of a pure substance or of
a eutectic mixture are present in equilibrium the temperature
must remain constant until one or other has disappeared. At
T_2 a flat portion SU of the curve therefore appears; at U all the
liquid has solidified and the mixture begins to fall again in
temperature.
    If a liquid mixture is taken with a composition nearer to the

eutectic composition than the liquid we have considered, the cooling curve will show the following differences:

(i) The temperature T_1 will come closer to T_2, which is the same for all mixtures.

(ii) The portion RS of the curve will be shorter, since there is less of the pure component to separate.

(iii) The flat portion SU—called the *eutectic arrest*—will be longer, since there is more eutectic to separate.

If one of the pure components is taken, the portion RS of the curve becomes long and horizontal and SU disappears, since the melting- and freezing-points of pure substances coincide. In organic chemistry the melting-point, and also the boiling-point under standard pressure, are widely used as criteria of purity, since the addition of foreign substances causes an apparent change in both these constants. If the substance is known to be pure, these constants are also frequently used to establish its identity. The conclusive test is to mix some of the substance with a pure sample of what it is believed to be: if the supposition is correct there will be no change in the melting- or boiling-point, but if a mistake has been made a change will be observed.

Effect of Compound-formation.—If the two components form a compound a rather different type of curve is obtained. In the diagram (Fig. 53) A and B are the melting-points of the components, while C is the melting‑point of the compound, which may be either above or below the melting-points of either of the components. D is the eutectic (I) between A and the compound, F the eutectic (II) between the compound and B. The liquidus is ADCFB, the solidus ALMCNPB. It is simplest to divide
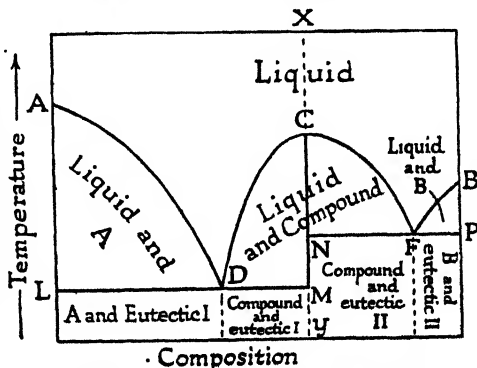
FIG. 53. FORMATION OF A COMPOUND: PHASE DIAGRAM

the system down the line XY into two two-component systems, one containing A and the compound, the other the compound and B: this has been done in Fig. 54. It must, however, be remembered that there is no discontinuity in the curve at C.

If the components form more than one compound there will be more than one hump in the curve. Metals often form a series
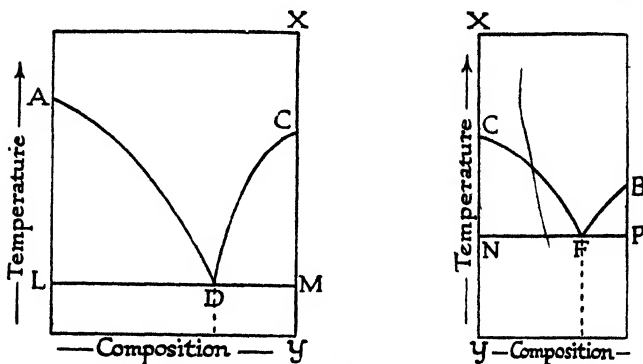
FIG. 54. FORMATION OF A COMPOUND: PHASE DIAGRAM

of such compounds, whose isolation is a matter of difficulty. Consequently phase diagrams are much used in the investigation of alloys; the conclusions can be confirmed by microscopic examination of a section. Fig. 55 is a photomicrograph of an etched section of an alloy of lead and tin. The crystals of tin, which appear white in the photograph, are separated from each other by the eutectic mixture, which appears black. The original melted alloy mixture was evidently richer in tin than the liquid eutectic mixture. Hence pure tin crystallizes until the eutectic temperature is reached, when minute crystals of lead and tin, closely interwoven, are simultaneously deposited between the crystals of tin. The phase rule interpretation of this solid is that it is simply a mixture, in two phases, of tin and lead. The appearance, however, is that of a mixture of (solidified) eutectic and tin. This segregation of 'eutectic' is of great importance in determining the properties of alloys, but in theory arises only because of the low

FIG. 55. PHOTOMICROGRAPH OF AN ALLOY OF LEAD AND TIN

rate of diffusion in the solid phase. It is in this sense that the descriptions of the solid phases introduced in Figs. 51 and 53 are to be understood.

Eutectic mixtures and constant-boiling mixtures have the following properties:

(i) Their melting- and freezing-points (or boiling- and condensing-points as the case may be) are identical.

(ii) They have constant composition, at constant pressure.

These properties have on several occasions led to the suggestion that they really are compounds. This suggestion can be conclusively disproved by a study of the effect of pressure, which changes both the melting and boiling-points and the composition of the eutectic. Since the effect of pressure on the properties of solids (e.g. alloys) is always very slight, the criterion is not always easy to apply, but any variation in composition from simple atomic ratios can be taken to suggest the presence of a eutectic mixture.

Effect of Mixed-crystal Formation.—If the components form mixed crystals in all proportions an entirely different phase diagram is obtained (Fig. 56). Since the components are completely miscible there are only two phases, one liquid and one solid. The diagram
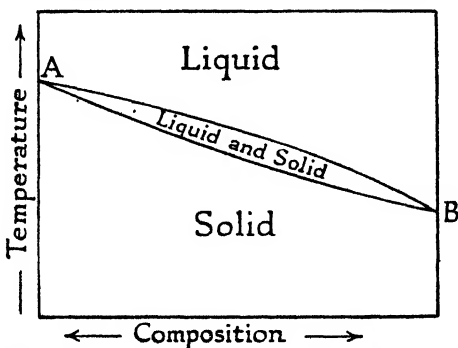
FIG. 56. TWO COMPLETELY MISCIBLE SOLIDS: PHASE DIAGRAM

therefore bears a striking resemblance to Fig. 45, which shows a liquid-vapour system, and the curves can be described on similar lines. Solid-liquid systems are also known similar to the liquid-vapour systems represented by Fig. 46, and in these the solidus and liquidus have a common minimum or maximum. The latter case is curious, since the addition of either component to the other raises the melting-point instead of lowering it: such systems are, however, very uncommon.

It frequently happens that the components form mixed crystals over a limited range of composition. The diagram (Fig. 57) shows the behaviour of two components, A and B, which behave in this fashion, and from what has been said already should be self-explanatory. L represents the composition of a saturated solution of B in A, M the composition of a saturated solution of A in B. Relationships of this type are very common between the metals, but the complications caused by the variation of the mutual solubility with temperature (compare the discussion of two partially
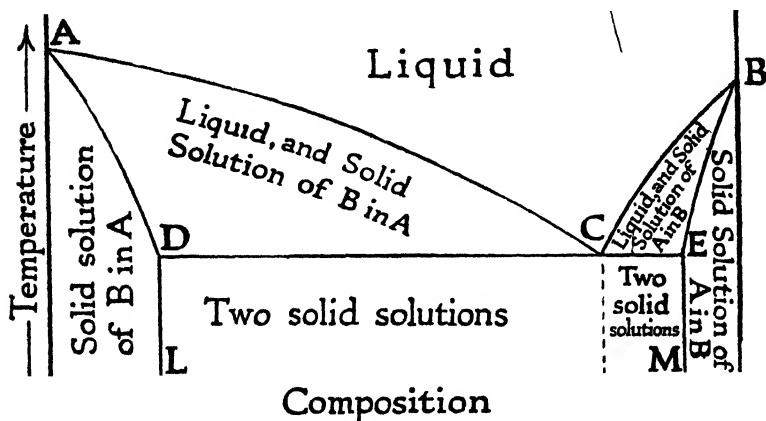
FIG. 57. TWO PARTIALLY MISCIBLE SOLIDS: PHASE DIAGRAM

miscible liquids on p. 171) cannot be considered here. In the diagram the mutual solubility is shown as independent of the temperature.

It has been pointed out by RIVETT in his book on the phase rule that the simple diagram (Fig. 51) showing no solid solutions is a limiting case of Fig. 57 which, strictly speaking, could never occur. Since, however, the mutual miscibility of many solids is so small as to escape detection, the simpler diagram may safely be used for any system in which the deviations of AD and BE from the vertical are too small to be measured.

Freezing-mixtures.—Before leaving the subject of two-component systems in the solid and liquid phases we may allude to the formation of freezing-mixtures made by mixing salts with ice or snow. These systems can be clearly understood only if it is realized that there is no essential distinction between solubility- and freezing-point curves, since both indicate the temperature at which solid may be expected to separate from the liquid phase. Thus if

potassium chloride is added to ice the temperature falls until it reaches the eutectic (or so-called 'cryohydric') temperature at —11° C., when the mixture contains 20 per cent of salt. A solution containing a larger proportion of salt than this begins to freeze at a higher temperature, and the solid which it deposits is not ice but salt. The curve CD (Fig. 58) is therefore the bottom part of the solubility-curve of the salt in water; any discontinuities it may show are due to the formation of hydrates. There is, in fact, no essential difference of type between the curves AC and DC. The
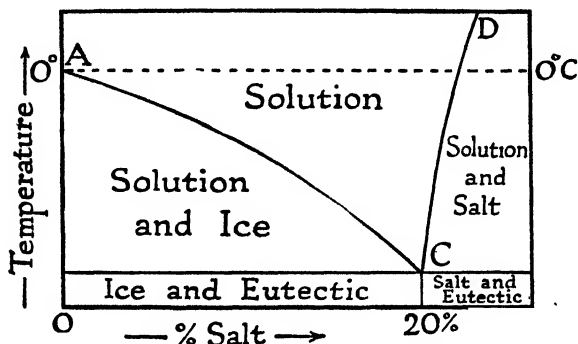
FIG. 58. FREEZING-MIXTURE: PHASE DIAGRAM

student should now revert to the ferric chloride solubility diagram in Chapter IV, p. 131, and see what new light is thrown on it by the phase-rule principles that we have discussed.

The Distribution Law.—In discussing from a qualitative aspect the subject of heterogeneous equilibrium we have hitherto been guided chiefly by the phase rule. The *Distribution Law* (sometimes called the *Partition Law*) is a generalization of almost equal importance and of a quantitative kind. Established experimentally by various workers for different systems, it was first put into a general form by NERNST in 1891, and has since been of the greatest service in the investigation of chemical equilibrium. It may be stated as follows: *A substance divides itself between two phases in such a way that the ratio of its concentrations in each phase is constant, provided that it is present in each phase in the same molecular species.*

We shall consider first the type of system to which the distribution law is most often applied—that of a solute in two immiscible (or only slightly miscible) liquids. If the solute is called X and the liquids are called A and B, the law states that at equilibrium $\dfrac{\text{Conc. of X in A}}{\text{Conc. of X in B}}$=a constant. If a further quantity of X is added

to the system, it will divide itself between the solvents in such proportions that the constancy of this ratio is not disturbed.   The term ' molecular species ' refers to the atomicity of the molecule, or, better, of the solute particles in each solvent: thus if in solvent A the solute X were partially associated into molecules X_2, the law in its simple form could no longer be applied.

The distribution law may be regarded as a simple corollary of the law of mass-action, if we regard X dissolved in A and X dissolved in B as separate chemical individuals:

X dissolved in $A \rightleftharpoons X$ dissolved in B.

The rate of change from left to right is proportional to the concentration of X in A, from right to left the rate of change is proportional to the concentration of X in B.   At equilibrium these rates of change are equal, and the ratio of the concentrations is therefore a constant.

Applied to one-component solid-vapour and liquid-vapour systems, the law leads to relations with which we are already familiar.   Since the concentration of a gas may be represented by its density, which in turn is at constant temperature proportional to its pressure, and since the concentration or active mass of a solid or pure liquid is a constant (see the discussion of the law of mass-action), it follows that at constant temperature both liquids and solids have constant vapour pressures, a conclusion that may also be reached by the more general method of the phase rule. By an extension to two-component systems, HENRY's *Law* can be deduced, to the effect that the solubility of a gas in a liquid is proportional to its pressure above it.   In two-component solid-liquid systems we learn that the concentration of a given solid in a given solvent in equilibrium with the solid is a constant at a fixed temperature—this concentration simply represents the solubility.

Distribution in Concentrated Solutions.—In the discussion of the law of mass-action it was pointed out that at high concentrations considerable deviations from the law might be observed. The same applies to the distribution law, and no case is known in which the distribution ratio is quite constant up to saturation and in all circumstances. Generally speaking, the greater the concentration the greater the deviation from theory. To take the example of a solute distributed between two solvents: if the law were exactly obeyed up to saturation the distribution ratio could

Solvent A

X

X

Solvent B

be calculated from the ratio of the solubilities, since the saturated solutions must be in equilibrium.   But this calculation, if made, is successful only for very slightly soluble substances; others nearly always show considerable deviations in concentrated solutions.

Experimental Devices.—In modern work these difficulties are usually avoided by various devices. If the solute is volatile (e.g. iodine or bromine) the two solutions need not be brought into contact at all. If they both communicate with the same vapour, they will in time reach equilibrium. In this way the distribution of a volatile solute between two water phases can be measured without the necessity of using a second solvent. In an American apparatus called the *equilibrator* the same air is made to bubble through the solutions in turn by revolving the whole apparatus about an eccentric axis, and in other devices the common vapour phase is exhausted to facilitate the diffusion of the solute vapour. If for some reason a second solvent cannot be dispensed with, any disturbing effects due to its solubility in the first solvent may be compensated by bringing the two solutions to be tested into equilibrium with the same solution in the second solvent; they must then be in equilibrium with each other with respect to the common solute.

Effect of the Molecular Species.—Deviations of quite another kind, involving alteration in the molecular species, are of great importance, and must now be considered.   Suppose the solute X is associated in phase 2, in which it exists almost entirely in the form of molecules X_n, while in phase 1 the molecules are almost exclusively simple.   There are then two equilibria to consider: one between the phases and the other in phase 2.   For if equilibrium is reached there must be some common species, even if present only in very small amount (in one of the phases), and the simplest assumption is that phase 2 contains a concentration of single molecules negligible in comparison with the concentration of X_n. Call the concentrations a, b, and c, as shown in the diagram.   Then

Phase 1

$$X_{(a)}$$

$$X_n \rightleftharpoons n\ X$$

(b) (c)

Phase 2

Fig. 60.   Distribution of an Associated Substance between Two Phases

from the distribution law $\dfrac{a}{c} = K_1$, where K_1 is a constant, while

from the law of mass-action $\dfrac{b}{\_\_} = K_2$, where K_2 is a constant.   Hence

$\frac{a^n}{b}$=constant, and since c is negligible in comparison with b, we

may say $\frac{(\text{Conc. in phase 1})^n}{(\text{Conc. in phase 2})}$ =constant.   A good example of this

behaviour is afforded by benzoic acid in water and toluene. The acid is weak, and in water exists almost entirely in single molecules (dissociation can as a first approximation be neglected), but in toluene as double molecules. It is therefore found that

$$\frac{(\text{Conc. in water})^2}{(\text{Conc. in toluene})}$$

is a constant.   Since the general equation can be written:

n log (conc. in phase 1)=log constant+log (conc. in phase 2),

the experimental results of the investigation of such a system are usually converted to this form.   If the logs of the concentrations in the two phases are plotted against one another, the value of n can be read off from the slope of the line.

Combination with the Solvent.—In dilute solutions combination with the solvent will not affect the constancy of the distribution ratio, for in such solutions the active mass of the solvent may be considered to be a constant, and the equilibrium in the equation
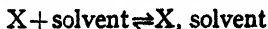
$$X + \text{solvent} \rightleftharpoons X, \text{solvent}$$

is therefore unaffected by dilution.   Since $\frac{[X]}{[X, \text{solvent}]}$ is a constant, the proportion of X combined with solvent is likewise constant, and neglect of this combination will alter only the magnitude of the distribution ratio as determined experimentally, not its constancy.

Dissociation.—If the solute is dissociated in one phase but not in the other no constant distribution ratio will be obtained, but the degree of dissociation can sometimes be calculated.   Suppose the substance X to dissociate in phase 2 into L and M, which may be ions or uncharged molecules, and let a be the degree of dissociation. Then *if the dissociation obeys the law of mass-action* we have, by reasoning similar to that already employed (see fig. 61):

$$\frac{a}{c}=K_1 \quad \frac{b^2}{c}=K_2 \quad \frac{b}{b+c}=a.$$

If the concentrations a and $(b+c)$ are determined by analysis, we have four equations and five unknowns, namely b, c, a, K_1, and K_2. These equations cannot be solved, but if we make another set of measurements at a different dilution we get four new equations and only three new unknowns (namely the new values of b, c, and a).

We have now eight equations and eight unknowns, and can solve them.   The method has two defects, viz.:

(i) that the dissociation of strong electrolytes does not obey the law of mass-action;

(ii) that the dissociation of weak electrolytes in solutions sufficiently concentrated for measurement is usually too small to be measured in this way.

Nevertheless, the method has yielded some highly important results, which will be briefly discussed below.

It must be remembered that distribution measurements give no information about the actual molecular condition in any phase, but merely indicate any difference there may be in the molecular condition in different phases.   In order to draw definite conclusions from such results, it is always necessary to measure the molecular weight in one phase or both by vapour-density or freezing-point determinations.   Caution must also be exercised in dealing with liquid-liquid systems in which the common solute may have any pronounced effect on the equilibrium between the solvents.   Thus the addition of hydrogen chloride increases the mutual solubility of ether and water to such a degree that distribution measurements of hydrogen chloride between these solvents would be very difficult to interpret.   A high mutual solubility of the two solvents is in any case always a disadvantage.

Phase 1

(a) X

$L + M \rightleftharpoons X$
(b) (b)   (c)

Phase 2

FIG. 61. DISTRIBUTION OF A DISSOCIATED SUBSTANCE BETWEEN TWO PHASES

Practical Applications.—We shall now briefly describe some of the applications of the distribution law to the problems of chemistry, under the following headings:

1. *Association;*
2. *Dissociation;*
3. *Extraction;*

while the important applications of the law to 4. *Complex ions* and 5. *Hydrolysis* will be considered under these headings in the next chapter.

1. *Association.*—The method has already been described.   In this way it has been shown that benzoic acid, acetic acid, and other substances are associated in various organic solvents, while lithium chloride is associated in amyl alcohol.

2. *Dissociation.*—In 1927 KNIGHT and HINSHELWOOD measured the distribution of hydrogen chloride between water and benzene, and in 1930 similar measurements were carried out by WYNNE-JONES on water and nitrobenzene (Fig. 62). He found that in solutions as concentrated as 8N practically the whole of the hydrogen chloride was in the water layer, while in dilute solutions the concentration in the nitrobenzene layer was so minute as to be difficult
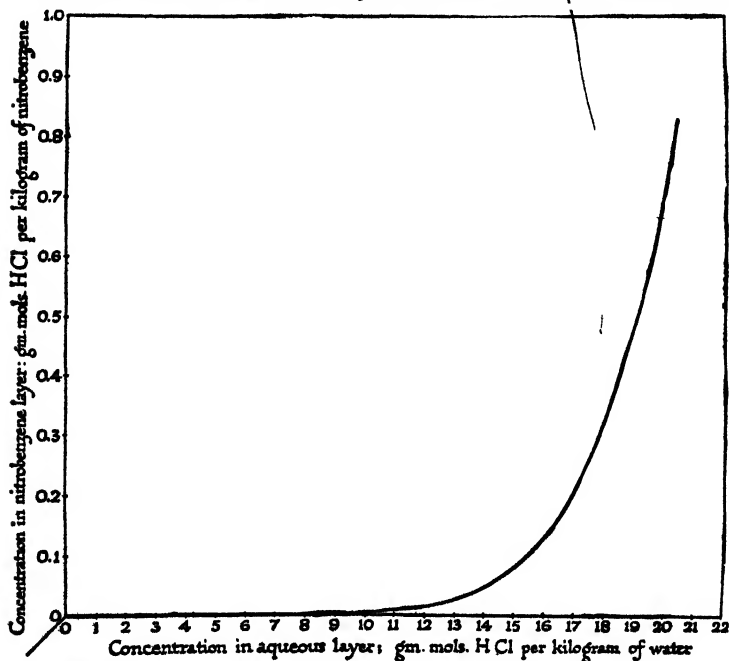
FIG. 62. DISTRIBUTION OF HYDROGEN CHLORIDE BETWEEN NITRO-BENZENE AND WATER (25°)

to detect. Since hydrogen chloride is very soluble in both liquids, and since the nitrobenzene solutions are known to contain some at least of the solute in the form of single molecules, it must be assumed that the concentration of single molecules in the water layer is negligibly small. Combination with the solvent cannot account for this effect, because, small as it is, the distribution-coefficient varies enormously with the concentration. The results therefore a striking confirmation, amounting almost to proof, of the theory of complete dissociation of strong electrolytes, and are all the more valuable because combination between solvent and

solute has on occasion been advanced as a tentative explanation of some of the other phenomena on which the ionic theory is based. The abnormally low vapour pressure of hydrogen chloride over its dilute aqueous solutions points in the same direction; it is so small that such solutions can be boiled for hours without appreciable loss of the acid.

HILL found that silver perchlorate (a strong electrolyte in water) was completely extracted by water from its solutions in benzene or toluene, but that aniline would extract it completely from water. With the base a relatively stable complex is produced. In the same way it has been suggested that the inability of carbon tetrachloride to extract any iodine monochloride from its solutions in aqueous hydrochloric acid points to the absence of any ICl molecules in the latter. Distribution measurements between toluene and water have been used to estimate the degree of dissociation of mercuric chloride, one of the small class of abnormal salts which are only slightly dissociated in water. The $HgCl_2$ molecules are soluble in toluene, but the ions $HgCl^{\cdot}$ and Cl' appear not to be capable of existence in that solvent. The results are in fair agreement with the law of mass-action.

3. *Extraction.*—In this process a solute is removed from a solution by shaking it with another solvent (immiscible with the first) in which it is more soluble: the favourable distribution ratio then causes most of it to pass into the latter. Extraction of aqueous solutions with ether is one of the commonest operations of organic chemistry, since most non-hydroxylic organic compounds are much more soluble in ether than in water. The process has the double advantage that it frees the solute from inorganic substances present in the aqueous solution (since these are nearly all insoluble in ether) and that the ether can be removed from the solute by evaporation at a lower temperature than the water, an important point when the solute is volatile or easily decomposed by heat. In inorganic chemistry such substances as iodine, bromine, sulphur, hydrogen peroxide, and ferric chloride can all be extracted from water by suitable solvents, and this is sometimes made use of in qualitative analysis. Given an aqueous solution and a fixed volume of solvent, e.g. ether, with which to extract it, it is then important to decide on the most efficient way of doing so. Suppose the volumes of water and ether are equal and that the distribution ratio of the substance to be extracted is 3 to 1 in favour of the ether. If we do the extraction in one operation we shall leave a quarter of the substance in the water, and our yield is only 75 per cent. If we divide the ether into four equal parts and extract with each part successively, our yields will be as follows:

From the first   extraction $\frac{3}{3+4} \times 100 = 43\%$, leaving 57% behind

„   „   second   „ $\frac{57}{100} \times \frac{3}{3+4} \times 100 = 24\%$ „   33%   „

„   „   third   „ $\frac{33}{100} \times \frac{3}{3+4} \times 100 = 14\%$ „   19%   „

„   „   last   „ $\frac{19}{100} \times \frac{3}{3+4} \times 100 = 8\%$ „   11%   „

By doing four extractions instead of one with the same total volume of ether we have therefore diminished the loss from 25 per cent to 11 per cent, and in general the more numerous the extractions the more efficient the process, but the number is in practice restricted by considerations of time and wastage.

Solvent A

X

X + y

Solvent B

FIG. 63. INVESTIGATION OF CHEMI-
CAL EQUILIBRIUM BY THE DIS-
TRIBUTION METHOD

4 and 5. *Other Equilibria in Solution.*—Examples of the application of the distribution law to other equilibria in solution will be given in the next chapter. Meanwhile we may explain the principle on which the measurements are based.

An equilibrium in solution $X + Y \rightleftharpoons Z$ cannot usually be investigated by analysing the amounts of X, Y, and Z present together, because as soon as one or other is removed for analysis the equilibrium is disturbed and more of this substance is produced. If, however, we can discover a second solvent immiscible with the first in which only one of the reactants or products (say X) is soluble, we can investigate the problem with the help of the distribution law. The distribution ratio of X between the two solvents must first be measured in experiments in which neither Y nor Z is present. The whole equilibrium is then investigated by determining the concentration of X in the solvent in which it alone dissolves when in equilibrium with the solvent containing the reaction mixture. The concentration of X in the latter can then be found by dividing (or multiplying) by the distribution ratio, and if the concentration of (Y+Z) is known our information complete. When the solvent A is added to the solvent B with the equilibrium already established in it, the equilibrium is

disturbed, and moves towards the left, owing to the removal of X. A new position of equilibrium is rapidly achieved, but of course the constant K is unaltered.

SUGGESTED FOR FURTHER READING

FINDLAY and CAMPBELL: *The Phase Rule and its Applications.*
RIVETT: *The Phase Rule.*
HILDEBRAND: *Solubility.*

HOMOGENEOUS EQUILIBRIUM

Ionic Equilibrium.—Our discussion of chemical equilibrium has for the most part been confined to reactions between molecules, except in the case of the dilution law of OSTWALD, which is generally applied to ions in low concentration in equilibrium with undissociated molecules. In this chapter we shall further consider the application of the law of mass-action to equilibrium between ions. Modern chemistry is so largely a chemistry of solutions—and aqueous solutions at that—that these applications have become of fundamental importance.

As an example of what is meant by an ionic equilibrium, we may take the reaction between solutions of ferrous sulphate and silver nitrate. If these solutions are mixed and allowed to reach equilibrium at a definite temperature (several hours are required), the following action takes place:

$$3FeSO_4 + 3AgNO_3 \rightleftharpoons 3Ag \downarrow + Fe_2(SO_4)_3 + Fe(NO_3)_3.$$
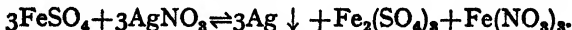
In the same way, if silver is shaken with ferric sulphate solutions, some of the silver dissolves and some of the ferric iron is reduced to the ferrous state. The equation that we have used to express the change fails because it implies that the sulphate and nitrate play some part in the reaction, whereas any other anions can be snbstituted for them, provided that they do not introduce reactions of their own. The reaction is in fact between the iron and the silver. Such difficulties can be avoided by the use of ionic equations, which invariably introduce a simplification. The ionic equation is derived from the older form simply by eliminating ions that occur on both sides. In this change, if we suppose all the salts to be fully ionized, we may write the equation:

$$3Fe^{..} + 3SO_4'' + 3Ag^. + 3NO_3' \rightleftharpoons 3Ag \downarrow + 2Fe^{...} + 3SO_4'' + Fe^{..} + 3NO_3'$$
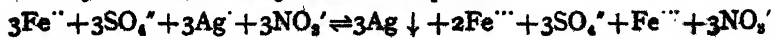
and this immediately reduces to:

$$Fe^{..} + Ag^. \rightleftharpoons Fe^{...} + Ag \downarrow ,$$

an equation free from the defect that has been mentioned. It implies that the change consists in the transfer of an electron from a ferrous ion to a silver ion, which thereby becomes an atom of silver and is precipitated, while the ferrous ion becomes a ferric ion. The reaction is one that can easily be subjected to experiment. If the law of mass-action is obeyed, the expression $\dfrac{[Fe^{..}]\,[Ag^{.}]}{[Fe^{...}]}$ should be a constant (since the active mass of the precipitated silver is a constant), and the values of this expression are in fact approximately constant at high dilutions. Very few cases are known in which the law of mass-action is exactly obeyed, either by neutral molecules or by ions, and ions obey it on the whole with rather greater divergences than neutral molecules. Nevertheless the law is sufficiently in accordance with experiment to be a useful quantitative guide in reasonably dilute solutions.

Solubility-product.—These ideas can be applied to 'insoluble' or slightly soluble salts. The equation representing the precipitation of barium sulphate from mixed solutions of any sulphate and any barium salt is:

$$Ba^{..}+SO_4^{''}\rightarrow BaSO_4\downarrow.$$
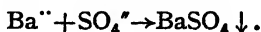
Since barium sulphate can be shown to have a slight solubility in water, the change is to some small extent reversible. If we apply the law of mass-action to the dissociation of the almost completely dissociated salt (and the very high dilution must be our justification) we get $\dfrac{[Ba^{..}]\,[SO_4^{''}]}{[BaSO_4]}=constant$, where $[BaSO_4]$ represents the minute concentration of undissociated barium sulphate in solution. Now in the presence of the solid, and at equilibrium, this must be a constant, whence $[Ba^{..}]\,[SO_4^{''}]$ must be a constant in solutions saturated with barium sulphate. This expression is called the *solubility-product*, and the solubility-product is approximately constant for a slightly soluble salt at a fixed temperature. Ionic concentrations are nearly always expressed in gram-formula-weights per litre, and the solubility expressed in the same way is equal to the square root of the solubility-product, provided the salt includes only two ions per formula-weight.

In order to give some idea of the degree of constancy which can be expected in the solubility-product we cannot do better than quote the results obtained by NERNST in 1889, two years after the enunciation of the ionic theory by ARRHENIUS. If the solubility-product really is constant, the apparent solubility of any slightly soluble salt will be reduced by the addition to the solution of any salt with a common ion. It was widely known that this was generally true, but Nernst decided to carry out a

quantitative test. He therefore determined the solubility of the slightly soluble salt silver acetate in strong solutions of silver nitrate and sodium acetate, and obtained the following results:

[Ag˙]	[Ac′]	[Ag˙] [Ac′]
0·0603	0·0603	0·0036
0·1027	0·0417	0·0043
0·1531	0·0341	0·0052
0·2495	0·0195	0·0049
0·0392	0·1002	0·0039
0·0280	0·1470	0·0041
0·0208	0·2508	0·0052

More favourable results could be quoted from modern work, but those given are interesting because they were the first measurements of the kind.   Notice that the biggest deviations from theory occur in solutions in which one of the ions is present in fairly high concentration—M/4—and this is generally true of solubility-product determinations.   Since the calculations are usually applied to salts much less soluble than silver acetate, agreement with theory is very often more satisfactory than in the measurements here quoted, and as we shall presently see, in the study of precipitations a variation of several hundred per cent in the solubility-product will frequently make no difference detectable by experiment.

Two simple examples of these ideas may be given:

1. Common salt may be precipitated from its concentrated solutions by passing hydrogen chloride into them.   This is a well-known method of freeing it from bromides and iodides, but it must be pointed out that in addition to the solubility principle another effect is at work—the hydrogen chloride combines with the water and renders some of it incapable of acting as a solvent. That this ‘ dehydrating ’ effect is very important is shown by the fact that cold concentrated sulphuric acid precipitates sodium *chloride* as readily as does hydrogen chloride.

2. Sodium carbonate can be partially converted to caustic soda by prolonged boiling with lime.   The reaction is:

$$Ca(OH)_2 \downarrow + CO_2'' \rightleftharpoons CaCO_3 \downarrow + 2OH',$$
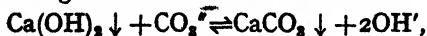
and at equilibrium the solution is saturated with both of the slightly soluble substances calcium hydroxide and calcium carbonate.   Let $[Ca``] [OH']^2 = K_1$, and $[Ca``] [CO_3''] = K_2$, then $\dfrac{[OH']^2}{[CO_3'']} = \dfrac{K_1}{K_2}$.   The reaction will therefore proceed until this condition is fulfilled, and as the solubility-product of calcium carbonate is much smaller than that of calcium hydroxide, the transformation can be carried out with some success.

The idea of the solubility-product can be applied to all solvents, but before considering in greater detail its applications to aqueous solutions we shall examine some of the peculiarities of water as a solvent, and particularly its ionization.

Ionization of Water.—That water is ionized follows from the fact that its electrical conductivity cannot be indefinitely reduced by the removal of impurities, but tends to a minimum value. That its ionization is extremely small follows from the very low value of this conductivity. The purest water ever produced was obtained in small yield by KOHLRAUSCH and HEYDWEILLER after nineteen distillations in a platinum apparatus. When transferred to a glass conductivity cell (which had been kept filled with conductivity-water for ten years to remove soluble impurities) it was found to have a specific conductivity of 0·043 reciprocal megohms at 18°. Assuming the dissociation to be $H_2O \rightleftharpoons H^{\cdot} + OH'$, and knowing the values of the mobilities of the hydrogen and hydroxyl ions as deduced from conductivity measurements, we obtain $[H^{\cdot}] = [OH']$ $= 0·78 \times 10^{-7}$. The law of mass-action can be applied to so minute a dissociation, and since the active mass of the undissociated water (owing to its enormous preponderance) is a constant, we may write $[H^{\cdot}][OH'] = 0·61 \times 10^{-14}$. The value of $[H^{\cdot}][OH']$ is called the *ionic product of water* and is usually denoted by K_w. The best values of this constant, obtained by the methods which will be discussed in due course, are:

°C.	0	18	25	50	100
$K_w \times 10^{14}$	0·12	0·59	1·04	5·50	51·3

THE IONIC PRODUCT OF WATER

From these figures it appears that in pure water at 25° only one-ten-millionth of the molecules are at any moment dissociated; its low conductivity is therefore not surprising. The four principal methods of calculating the ionic product of water are as follows:

   (i) From the conductivity of pure water, as above.

  (ii) From the catalytic effect of hydrogen and hydroxyl ions (p. 212).

 (iii) From measurements of hydrolysis (p. 203). The degree of hydrolysis, as determined by experiment, is inserted in the equation (p. 204) connecting it with the ionic product of water and the dissociation-constant of the weak acid or base, which must be measured in separate experiments. The only unknown in this equation is then the ionic product of water, which can therefore be calculated.

 (iv) From E.M.F. measurements with a hydrogen electrode in acid and alkaline solutions (p. 258).

These methods all give concordant results.

G

Acids and Bases.—It is chiefly to the fact that they have an ion in common with water that acids and bases owe the peculiar properties in aqueous solution which make it necessary to consider them as separate classes of substances. Acids are usually taken to be substances that in aqueous solution liberate hydrogen ions, bases substances that in aqueous solution liberate hydroxyl ions. That acidic and basic properties are closely connected with the presence of water has been shown by many ingenious experiments. A solution of dry hydrogen chloride in dry toluene will not liberate carbon dioxide from marble, nor will it act on iron, but as soon as a drop of water is added action begins. The precise connection between acidity and the nature of the solvent is still obscure, and will be further discussed in the section on the electron theory of valency, but in the meantime, for want both of adequate theory and of experimental data upon which to base it, the discussion will be confined almost entirely to aqueous solutions, and we shall find no inconvenience in a definition of acidity in terms of water.

The chemical properties of acids are readily represented by this method. The solution of, say, zinc proceeds as follows:

$$Zn + 2H^{\cdot} \rightarrow Zn^{\cdot\cdot} + H_2 \uparrow ;$$

and of zinc oxide:

$$ZnO + 2H^{\cdot} \rightarrow Zn^{\cdot\cdot} + H_2O;$$
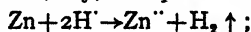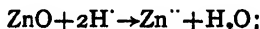
while the action on zinc carbonate is:

$$ZnCO_3 + 2H^{\cdot} \rightarrow Zn^{\cdot\cdot} + H_2CO_3, \text{ followed by } H_2CO_3 \rightleftharpoons CO_2 + H_2O.$$

Physico-chemical conceptions of what compounds may properly be classed as acids or bases have been much extended during the past thirty years, mainly owing to the initiative of LOWRY in England and BRÖNSTED in Denmark. The typical property of an acid A is taken to be represented by the forward direction of the equation

$$A \rightleftharpoons A' + H^{\cdot},$$
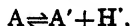
that is, an acid is regarded as a *proton donor*. A base B acts typically as a *proton acceptor*, according to the forward direction of the equation

$$B + H^{\cdot} \rightleftharpoons BH^{\cdot}.$$
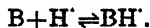
If this latter change occurs in aqueous solution, the removal of hydrogen ion will, in obedience to the equation

$$[H^{\cdot}][OH'] = K_w \text{ (see p. 191),}$$

cause the concentration of hydroxyl ion OH′ to rise; that is, the liquid becomes alkaline. The functions of acid and base are conjugated, for A′ is a base, and BH˙ is an acid. Chemical compounds yielding hydroxyl ions, such as sodium or potassium hydroxide, are

strictly not bases, but ' basigens,' for they liberate the true base OH'. Further, many compounds and ions not hitherto regarded as bases must according to these views be included in the class, e.g. acetate ion. Ammonia is included not on the doubtful ground of the formation of ammonium hydroxide NH_4OH, but because of the reaction

$$NH_3 + H^{\cdot} \rightleftharpoons NH_4^{\cdot}.$$
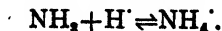
The class of acids must also be widened to include, for example, ammonium ion $NH_4^{\cdot}$. One advantage of this modern view is the great simplification possible in the explanation of salt hydrolysis (p. 204). We can say that sodium acetate yields an alkaline aqueous solution simply because it contains a base, acetate ion, and ammonium salts give acid solutions because they contain an acid, $NH_4^{\cdot}$. In dealing with non-aqueous liquids the facts can only be reduced to order by adopting such a broadened outlook as has been outlined. It must not be forgotten that suitable substances exhibit typical acidic and basic behaviour in benzene solution, wherein there can be no free existence of either hydrogen or hydroxyl ions. However, the practical chemist will no doubt hesitate to abandon the traditional ideas, which, it must be admitted, serve reasonably well for aqueous solutions. The new views lead to alternative ways of applying the law of mass-action to weak bases, such as ammonia, in aqueous solution: from the equation

$$NH_3 + H^{\cdot} \rightleftharpoons NH_4^{\cdot}$$

we derive the relation

$$\frac{[NH_4^{\cdot}]}{[NH_3][H^{\cdot}]} = K_b';$$

but in aqueous solutions we must always have $[H^{\cdot}][OH'] = K_w$: hence we find

$$\frac{[NH_4^{\cdot}][OH']}{[NH_3]} = K_w . K_b' = K_b^{\cdot}.$$

Heat of Neutralization.—The neutralization of a strong acid by a strong base is simply:

$$H^{\cdot} + OH' \rightarrow H_2O.$$
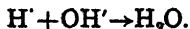
The same cannot be said of the neutralization of a weak acid by a weak base. The action of, say, acetic acid on ammonia must be written:

$$CH_3.COOH + NH_3 \rightarrow CH_3.COO' + NH_4^{\cdot},$$

and we are really concerned with two successive changes, $CH_3COOH \rightarrow CH_3COO' + H^{\cdot}$, and $NH_3 + H^{\cdot} \rightarrow NH_4^{\cdot}$. If these considerations are correct, the heat liberated when one gram-molecule of a strong acid neutralizes one gram-molecule of a strong base should be a

constant, since in every case the action is the same, whereas the heat of neutralization of weak acids or bases will include the heat change on dissociation and will therefore be variable. This has been experimentally verified, and the very close agreement between theory and experiment is strong evidence in favour of the dissociation theory.

Strong Acid	Base	Calories	Weak Acid	Base	Calories
HCl	KOH	13,750	$CH_3.COOH$	NaOH	13,230
HCl	NaOH	13,740	$CHCl_2.COOH$	NaOH	14,830
HNO_3	KOH	13,770	H_3PO_4	NaOH	14,830
HNO_3	NaOH	13,685	HF	NaOH	16,270

HEATS OF NEUTRALIZATION

For approximate calculations it is convenient to make K_W equal to 1×10^{-14} at 25°. The ionic product of water is a constant, hence the value of the hydroxyl ion concentration is in acid solutions depressed below the small value of 10^{-7} which it has in pure water, and the same applies to the hydrogen ion concentration of alkaline solutions. Since it may be assumed that strong acids and bases are completely dissociated in dilute aqueous solution, the calculation is an easy one. Thus a M/100 solution of hydrochloric acid has at 25° a hydrogen ion concentration of 10^{-2} and a hydroxyl ion concentration of 10^{-12}, while a M/1000 solution of caustic soda has a hydrogen ion concentration of 10^{-11} and a hydroxyl ion concentration of 10^{-3}. The *hydrogen ion concentration* occurs so frequently in calculations that a special symbol has been invented to represent it—p_H—equal to the $\log_{10}$ of the true concentration with the minus sign omitted. Thus p_H 4·5 indicates a hydrogen ion concentration of $10^{-4\cdot5}$, and so on.

As an exercise we may calculate the p_H value of a M/100 solution of acetic acid. The dissociation-constant of this acid is $1·85 \times 10^{-5}$, or $\dfrac{[H^·] [CH_3.COO']}{[CH_3.COOH]} = 1·85 \times 10^{-5}$. Since the hydrogen and acetate ions have both been derived from the acid, $[H^·] = [CH_3.COO']$, and since the degree of dissociation is obviously extremely small, we may without sensible error write $[CH_3.COOH] = \dfrac{1}{100} = 10^{-2}$. Hence $[H^·]^2 = 1·85 \times 10^{-7}$ or $[H^·] = 4·3 \times 10^{-4}$, or $= 10^{-3\cdot4}$, or, otherwise expressed, $p_H = 3·4$. The solution has about the same hydrogen ion concentration as a M/2,500 solution of hydrochloric acid.

Precipitation.—We are now in a position to study precipitation from a quantitative point of view, and may begin with hydrogen sulphide on account of its wide use in the laboratory, particularly

in analysis. Hydrogen sulphide is a weak dibasic acid which dissociates in two steps, the constants at 25° being approximately:

$$\frac{[H^{\cdot}]\,[HS']}{[H_2S]} = 10^{-7} \quad \text{and} \quad \frac{[H^{\cdot}]\,[S'']}{[HS']} = 10^{-15}$$

As we shall not consider any complications which may arise from the presence of the HS' ion, it may be eliminated at once by multiplying the equations together, obtaining the equation:

$$\frac{[H^{\cdot}]^2\,[S'']}{[H_2S]} = 10^{-22}$$

Hydrogen sulphide is therefore a very weak acid, and the concentration of the ions is negligible in comparison with that of the undissociated molecules. In an aqueous solution saturated at 25° and at atmospheric pressure, $[H_2S]$ is about 0·1, so that under these conditions $[H^{\cdot}]^2\,[S''] = 10^{-23}$. This equation controls the precipitation of metallic sulphides from aqueous solutions. Obviously the greater the hydrogen ion concentration (i.e. the acidity) the lower the sulphide ion concentration. High sulphide ion concentrations are only reached in alkaline solutions; this is because soluble metallic sulphides are largely dissociated, while hydrogen sulphide is not. Reaction with the water of the solution complicates the simple calculation, but it is possible to deduce the following values for the sulphide ion concentration of the solutions used in qualitative analysis:

M/10 $(NH_4)_2S$ . . . . 2×10^{-6}
Water, saturated at atmospheric pressure with H_2S . 10^{-15}
M/5 HCl 10^{-22}

As is well known, the salts of Cu, Cd, Ag, Pb, Hg, Bi, As, Sb, and Sn are precipitated from acid solutions by hydrogen sulphide, whereas the salts of other common metals are not. Taking M/10 as an average value of the concentration of the cation, supposed bivalent, we know that the solubility-product 0·1 $[S'']$ will just be reached when precipitation takes place. If, as above, the value of $[S'']$ in the acid solution is 10^{-22}, those metals will be precipitated in acid solution whose sulphides have a solubility-product less than 10^{-23}. This is true of most of the metals mentioned: thus the solubility-products of copper, mercuric, and silver sulphides are:

$[Cu^{\cdot\cdot}]\,[S''] = 10^{-42}$ $[Hg^{\cdot\cdot}]\,[S''] = 10^{-54}$ $[Ag^{\cdot}]^2\,[S''] = 10^{-50}$.

Other metals (e.g. zinc) can be precipitated as sulphides from alkaline but not from acid solutions, and their solubility-products lie between 2×10^{-6} and 10^{-22}. Some metals lie near the border-line and may be placed in the wrong class if the acid concentration

is not carefully adjusted. Solutions of cadmium salts in strong hydrochloric acid are not precipitated by hydrogen sulphide, whereas zinc salts may come down if the acid concentration is not high enough; this is because the solubility-product of cadmium sulphide is only a little less than 10^{-22} and that of zinc sulphide only a little more. Such a reduction in the hydrogen ion concentration may arise unexpectedly if the anion of a weak acid is present in the solution, because this anion absorbs the added hydrogen ions, which are then not available to repress the ionization of the hydrogen sulphide. When, for example, dilute hydrochloric acid is added to a solution of zinc acetate the hydrogen ions of the acid form the very slightly dissociated substance acetic acid with the acetate ions, leaving the hydrogen ion concentration of the solution not much affected, and if the hydrochloric acid is not added in sufficient quantity to overcome this effect, zinc sulphide will be precipitated from the solution by hydrogen sulphide.

Similar considerations apply to precipitations with ammonia. We have seen that the equilibrium equation may be written $\frac{[NH_4^{\cdot}]\,[OH']}{[NH_3]}=K$, where $[NH_3]$ represents the concentration of the total ammonia dissolved in the solution. The value of the constant is about $1\cdot8\times10^{-5}$, so that in a M/2 solution of ammonia $[NH_4^{\cdot}]=[OH']=\sqrt{0\cdot5\times1\cdot8\times10^{-5}}=3\times10^{-3}$. From this we can see which metallic hydroxides will be precipitated by such a solution. Take magnesium as an example. In a M/5 solution of magnesium chloride $[Mg^{\cdot\cdot}]$ is about $0\cdot2$, so that, if the solution is at the same time M/2 in ammonia, $[Mg^{\cdot\cdot}]\,[OH']^2=0\cdot2\times(3\times10^{-3})^2=1\cdot8\times10^{-6}$. This is greatly in excess of the solubility-product of magnesium hydroxide $(1\cdot5\times10^{-11})$, which will therefore be precipitated. The precipitation, however, as is well known in qualitative analysis, can be prevented by the addition of a sufficient excess of ammonium chloride. The effect of this substance is to drive back the reaction $NH_3+H^{\cdot}\rightleftharpoons NH_4^{\cdot}$ to the left by providing an excess of ammonium ions. Suppose the solution is 2M in ammonium chloride. Then $[NH_4^{\cdot}]=2$, $[NH_3]$ as before is $0\cdot5$, and consequently $[OH']=\frac{1\cdot8\times10^{-5}\times0\cdot5}{2}=4\cdot5\times10^{-6}$. Then $[Mg^{\cdot\cdot}]\,[OH']^2=0\cdot2\times(4\cdot5\times10^{-6})^2$

$=0\cdot4\times10^{-12}$. This is below the solubility-product of magnesium hydroxide, which should therefore not be precipitated. The older y that the precipitation of magnesium hydroxide is prevented the addition of ammonium chloride on account of the formation double salts, though demonstrably incorrect, is still found in some rks on analysis.

cipitations with carbon dioxide can be treated in the same

way. *Thus calcium carbonate cannot be precipitated by carbon* dioxide from calcium chloride solutions because the concentration *of carbonate ions from the reaction* $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons 2H^{\cdot} + CO_3''$ is never sufficiently great for the solubility-product $[Ca^{\cdot\cdot}]\,[CO_3'']$ to be exceeded. But it can be precipitated from solutions of calcium hydroxide ('lime-water') because the hydroxyl ions combine with the hydrogen ions provided by the carbonic acid and cause it to dissociate further, thus producing carbonate ions in sufficient concentration for precipitation to take place.

Double Salts.—The nature of the ions that a salt will furnish in solution is not always obvious from inspection of the formula, and must be decided by experiments on the solution. Salts containing more than one possible anion or cation can be divided into two classes: the so-called *double salts* and *complex salts*. The former give in solution the reactions of all the ions of their constituent salts, the latter may not.

As an example of a double salt we may give the well-known compound ferrous ammonium sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$, which can be precipitated from suitably concentrated solutions of ferrous sulphate and ammonium sulphate. In solution it gives the reactions for the following ions: $NH_4^{\cdot}$, $Fe^{\cdot\cdot}$, and SO_4'', and its solutions cannot be distinguished from solutions of its constituents mixed in equimolecular proportions. The formation of double salts probably depends on space relations in the crystal: if the ions fit easily into the lattice together, a double salt may be produced. Such substances must, however, be distinguished from solid solutions or mixed crystals in which the points of the lattice are indifferently occupied by one ion or the other. Double salts are true compounds and the arrangement of the ions within the lattice is identical in all parts of the crystal, while the criterion of invariable composition is always observed.

Complex Salts.—Complex salts do not give all the ions of their constituents in solution. If silver cyanide is dissolved in a solution of potassium cyanide, no precipitate of silver chloride can be obtained on the addition of a soluble chloride. The potassium ions are still present, but the silver ions are no longer in evidence, though means are known of demonstrating their presence in minute concentration. The vast majority of them have been absorbed to form argentocyanide ions in accordance with the equation $Ag^{\cdot} + 2CN' \rightleftharpoons Ag(CN)_2'$. Other well-known examples of complex ions are the ferrocyanide $Fe(CN)_6''''$ and the ferricyanide $Fe(CN)_6'''$, produced by the union of six cyanide ions (CN') with a ferrous or ferric ion. Complex ions are of very great importance in solution chemistry, and we shall therefore give a general account of their peculiarities.

Methods of Investigating Complex Ions.—There is no sharp

distinction between complex ions like ammonium or ferrocyanide —which are so stable that it is difficult to demonstrate the presence of their constituents in their solutions—and such complexes as hydrated ions (e.g. $Co.6H_2O$''), which decompose comparatively easily. Generally speaking, complex ions of all classes are quite as stable in the solid state as in solution, and in the crystal they can often be detected by the ordinary methods of X-ray analysis. We shall now describe the principal methods of detecting complex ions in solution and of estimating their concentration.

1. *Chemical Tests for Constituents.*—When ammonia is added to a solution of silver nitrate, the precipitate of silver oxide dissolves in excess of ammonia, and if enough ammonia is present, considerable quantities of potassium chloride can be added without producing a precipitate of silver chloride. By making the experiment quantitative and carrying it out under various conditions of concentration it can be shown that the complex has been formed by the union of one silver ion with two molecules of ammonia: $Ag^{\cdot}+2NH_3 \rightleftharpoons Ag.2NH_3^{\cdot}$, and that the equilibrium equation is $\dfrac{[Ag^{\cdot}][NH_3]^2}{[Ag.2NH_3^{\cdot}]}=7\times10^{-8}$ at 25°. The equilibrium lies so far to the right that in dilute chloride solutions the solubility-product of silver chloride is not exceeded, as can easily be seen by calculation ($[Ag^{\cdot}][Cl']=2\times10^{-10}$). But silver bromide is so much less soluble than silver chloride that a far smaller concentration of potassium bromide will produce a precipitate, while silver iodide, the least soluble of the three, is precipitated in very low iodide concentrations. This method can be used to separate silver chloride from silver iodide. The usual explanation is that ' silver chloride is more soluble in ammonia than silver iodide,' but this is not a satisfactory way of stating the facts.

Both the silver ion and the ammonia molecules have had their properties entirely changed by combination. The compound $AgCl.2NH_3$ is well known in the solid state, and is soluble in water, while its aqueous solution has strong basic properties, contrasting with the only weakly basic properties of ammonia.

Both cyanide ions and ammonia molecules form stable complex ions with many of the metals. This property will be explained in Chapter XI. Among the best-known cyanide complexes are those with Cu, Ag, Au, Zn, Cd, Hg, Fe, Co, Ni, while the metals forming ammonia complexes include Cu, Ag, Zn, Cd, Ni. The composition and stability of these ions are very various. The relative stability of the copper and cadmium cyanide complexes is beautifully demonstrated in the analytical process for their separation. When the mixed copper and cadmium solutions have been treated with

potassium cyanide nearly all the copper is present in the cuprous condition as the very stable ion $Cu(CN)_3''$, while some of the cadmium is present as $Cd(CN)_4''$. That the cupric ions have disappeared is evident from the colourless solution. If now ammonium sulphide is added to the mixture, a precipitate consisting entirely of the bright yellow cadmium sulphide is obtained. In spite of its very low solubility, copper sulphide cannot be precipitated from the cyanide solutions because they contain practically no copper ions, whereas the cadmium complex is less stable.

FEHLING'S solution, so well known in organic chemistry, is a mixture of copper sulphate, sodium potassium tartrate, and excess of caustic soda. Since the solution is perfectly stable, containing a large excess of hydroxyl ions but giving no precipitate of cupric hydroxide, it must contain the copper in a complex ion. The formula of the latter is $Cu(C_4H_4O_6)_2''$, and its colour dark blue. Copper sulphide can be precipitated from it with ammonium sulphide.

2. *Abnormally High Solubility.*—When substances insoluble in water show considerable solubility in a solution with which they are not known to undergo a chemical reaction, the formation of complexes may be inferred. We have already discussed the solubility of silver chloride in ammonia; similarly all silver salts will dissolve in cyanide solutions, the complexes $Ag(CN)_2'$ and $Ag(CN)_3''$ being, with the ferro- and ferricyanides, among the most stable cyanide complexes known. Even the highly insoluble silver sulphide ($[Ag']^2 [S''] = 10^{-50}$) will dissolve in concentrated cyanide solutions, and for this reason potassium cyanide is sometimes found as an ingredient in plate-powders, though its use for this purpose is exceedingly dangerous.

Mercuric oxide, though very insoluble in water, dissolves slightly in bromide solutions and readily in iodide solutions. Measurements of the solubility show that the action is $HgO \downarrow + 4I' + H_2O \rightleftharpoons HgI_4''$ $+ 2OH'$ and that the equilibrium expression $\dfrac{[HgI_4''] [OH']^2}{[I']^4}$ is fairly constant in dilute solutions. (Since two hydroxyl ions are produced for every molecule of mercuric oxide that dissolves, the process is sometimes used in preparing solutions of standard alkalinity: a weighed quantity of the oxide is dissolved in excess of potassium iodide solution and the solution used for the standardization of acids.) For the same reason, when excess of potassium iodide is added to the solution of a mercuric salt, the scarlet precipitate of mercuric iodide that is at first produced readily dissolves in excess to give a colourless solution:

(i) $Hg'' + 2I' \rightarrow HgI_2 \downarrow$
  scarlet

(ii) $HgI_2 \downarrow + 2I' \rightarrow HgI_4''$
  scarlet   colourless
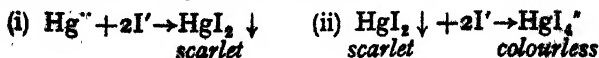
Similar considerations apply to the solubility of cupric hydroxide in excess of ammonia to form the distinctive deep blue colour of the copper - ammonia ion (or ions). Quantitative investigation of the system is difficult because some of the cupric hydroxide is in colloidal solution. In the presence of excess of ammonia the ion is chiefly $Cu.4NH_3^{..}$ (cf. p. 201).

Iodine, though only very slightly soluble in water, is much more soluble in hydrochloric acid. The diagram (Fig. 64) shows that the relation between iodine solubility and acid concentration is a linear one. The point A represents the solubility in pure water. Distribution measurements similar to those described in the next

FIG. 64. SOLUBILITY OF IODINE IN HYDROCHLORIC ACID

section show that the complex is CII_2'. Hence $\dfrac{[Cl'] \, [I_2]}{[CII_2']}$ is constant, and if we assume that the increased solubility is entirely due to the formation of this complex ion the linear solubility relation follows at once, since $[CII_2']$ is negligible compared with $[Cl']$.

3. *Distribution Method.*—This is one of the oldest and most successful methods of investigating complexes, and has been used since the nineties to examine the complexes formed between iodine and halide ions. The stability of these complexes increases in the order chloride, bromide, iodide; and the solubility of iodine in solutions of potassium iodide is put to constant use in the laboratory.

FIG. 65. DISTRIBUTION OF IODINE BETWEEN BENZENE AND AQUEOUS POTASSIUM IODIDE

If these solutions are shaken up with a solvent such as benzene or carbon tetrachloride, immiscible with water, some of the iodine is extracted from the aqueous layer, but none of the ions (Fig. 65). Iodine

is known to exist exclusively as diatomic molecules in both water and benzene, and consequently has a nearly constant distribution ratio between these solvents in the absence of complex-forming substances. By dividing the concentration in the benzene layer by this ratio it is therefore possible to calculate the concentration of iodine as I_2 in the potassium iodide solution, and if the total concentration as I_2 and I_3' is known, the concentrations can be inserted in the equation $\dfrac{[I_2]\,[I']}{[I_3']}=$ constant. This test is found to give satisfactory results, whereas alternative proposals, such as

$$I_2+2I'\rightleftharpoons I_4'' \qquad \text{or} \qquad 2I_2+I'\rightleftharpoons I_5',$$
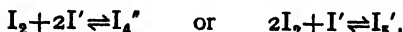
give unfavourable ones. It is perhaps necessary to make it clear that the direct chemical method of investigating the equilibrium is bound to fail, since on analysis with thiosulphate, for example, the tri-iodide ion progressively decomposes as the iodine is removed.

Similar methods have been used in examining by distribution experiments with chloroform the copper-ammonia complex ion in the presence of excess of ammonia. The diagram (Fig. 66) makes the method clear.
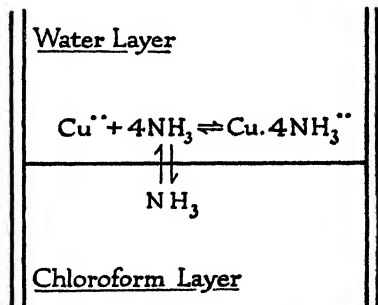
FIG. 66. DISTRIBUTION OF AMMONIA BETWEEN CHLOROFORM AND A COPPER SULPHATE SOLUTION

4. *Conductivity Method.*—The changes in the electrical conductivity of solutions that complex formation brings about sometimes provide useful evidence. Thus the addition of stannic chloride to hydrochloric acid reduces the conductivity considerably, a fact which points to the formation of a chloro-stannate (p. 605) or some other complex: $SnCl_4+2Cl'\rightleftharpoons SnCl_6''$. The decrease in conductivity may be taken to indicate a decrease in the number of ions in the solution. Conductivity found its chief application in this field when Werner used it to elucidate the structures of the complex salts of cobalt, platinum, and other metals. These substances are more complicated than any we have hitherto considered and will receive fuller treatment later on when their structure is discussed (Chapter XI). Meanwhile we may briefly examine the series of substances, all containing bivalent platinum, whose formulae may be written: (1) $Pt.4NH_3.Cl_2$; (2) $Pt.3NH_3.Cl_2$; (3) $Pt.2NH_3.Cl_2$; (4) $K.Pt.NH_3.Cl_3$;

(5) K_2PtCl_4. In the diagram (Fig. 67) their molecular conductivities at equal dilution are arranged in order. Since No. (3) does not conduct at all, it does not furnish any ions in solution, and the order of the conductivities of the remainder leads one to suppose that Nos. (2) and (4) have two ions each and Nos. (1) and (5) three each. The formulae are therefore tentatively written: (1) $[Pt.4NH_3]^{++}2Cl^-$; (2) $[Pt.3NH_3.Cl]^+Cl^-$; (3) $Pt.2NH_3.Cl_2$; (4) $K^+[Pt.NH_3.Cl_3]^-$; (5) $2K^+[PtCl_4]^{--}$. At this point we notice (a) that the charges are

FIG. 67. CONDUCTIVITY OF
COMPLEX SALTS

correct, each platinum ion (-ous) contributing two positives, each chlorine ion one negative, and the ammonia molecules nothing; (b) that this arrangement gives four ammonia molecules or chlorine atoms to every platinum atom. This regularity suggests that we are on the right track, and our views can be confirmed by chemical tests for the ions alleged to be present. Thus Nos. (1) and (2) are the only salts that give a precipitate of silver chloride with silver nitrate, and in (1) the whole of the chlorine in the compound can be thus precipitated, in (2), however, only half of it.

5. *Transport Numbers.*—Abnormal transport numbers generally indicate complex formation, and unusually wide variations with dilution are specially significant. HITTORF passed an electric current through a strong solution of cadmium iodide and then measured the concentrations of cadmium and iodide near the electrodes. He found that electrolysis made little difference to the concentration of cadmium round the cathode, whereas a large increase might be expected, since when the current is passing all positive ions move in this direction. On the other hand, the iodide concentration round the cathode had suffered a quite abnormal decrease. At high concentrations the Hittorf transport number of the cadmium was in fact negative, the iodine transport number greater than one. The explanation of these anomalous results is as follows. Concentrated cadmium iodide solutions form ions CdI_4'' which travel to the anode, each double charge being associated with four iodine atoms instead of the normal two, whereas for each cadmium atom carried in this way to the anode a normal cadmium ion Cd'' travels to the cathode. Since these complexes tend to break up with increasing dilution, the transport numbers also approach normality in dilute solutions. This type of auto-complex formation is also shown by the halides of the related elements zinc and mercury. Increase in concentration always increases the

proportion of complex ions in a solution containing auto-complexes, since auto-complex formation reduces the total number of ions, e.g.:

$$Cd^{\cdot\cdot} + 4I' \rightleftharpoons CdI_4''.$$
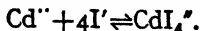
6. *Freezing-point Method.*—When iodine is added to excess of an aqueous solution of hydrogen iodide the freezing-point of the acid solution remains unchanged. Since the freezing-point lowering is a measure of the number of particles per c.c. of solution, it follows that the addition of the iodine has left this number unchanged. The observation is in conformity with the changes $I_2 + I' \rightleftharpoons I_3'$ or $2I_2 + I' \rightleftharpoons I_5'$, but not with the changes $I_2 + 2I' \rightleftharpoons I_4''$ or $I_2 + 3I' \rightleftharpoons I_5'''$. Other methods have shown that the first suggestion is the correct one.

7. *Colour of the Solutions.*—Many complex ions are strongly coloured. Such are the blue copper-ammonia and nickel-ammonia ions, and the innumerable complex ions containing cobalt. On the other hand the cuprocyanides are distinguished from cupric salts by their lack of colour. By spectroscopic determinations of the depth of colour it is possible to make estimates of the concentration of the complex present. An interesting example is afforded by the red and blue solutions of cobalt chloride. If the ordinary red solution of this salt is evaporated it gradually becomes blue as the concentration increases, and in recent years it has been suggested that the blue ions are $Co.4H_2O^{\cdot\cdot}$ and the red ones $Co.6H_2O^{\cdot\cdot}$. But the question is complicated by the presence of $CoCl_4''$ and possibly other ions, and has not yet been definitely settled. It is also possible to measure absorption in the ultraviolet part of the spectrum, to which water is nearly transparent, and work of this kind has confirmed the existence of the tri-iodide ion.

8. *Electrode Potential Method.*—A discussion of this method must be deferred to Chapter VIII (p. 261).

Hydrolysis.—Having discussed reactions that may occur between solute ions we must consider the actions that may take place between solute ions and the ions of the water itself. This restriction of the discussion to water is unfortunately made necessary by our comparative ignorance of other solvents, but a short account of reactions in liquid ammonia will be found in the section dealing with that solvent (p. 393).

Certain types of reaction between water and substances dissolved in it are denoted by the general name of *hydrolysis*. As its form implies the term hydrolysis should be restricted to those reactions in which there is a separation of the hydrolysed substance into at least two parts: equation (*a*) represents the hydrolysis of chlorine, and equation (*b*) its *hydration*.

$$Cl_2 + H_2O = HClO + H^{\cdot} + Cl' \quad (a)$$
$$Cl_2 + 8H_2O = Cl_2.8H_2O \quad (b).$$
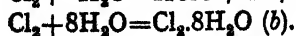
Hydrolysis of salts can take place only when one of the ions of the solute is the anion of a weak acid or the cation of a weak base. Since a weak acid or a weak base is a substance whose molecules are only slightly dissociated in water, these ions will have the power of drawing hydrogen or hydroxyl ions respectively from the water to form the corresponding undissociated molecules. An excess of hydroxyl or hydrogen ions is thus left in the solution, which therefore becomes alkaline or acidic, and this is the essential feature of salt hydrolysis. Solutions of salts of strong acids and weak bases are acidic, solutions of salts of weak acids and strong bases are alkaline. Solutions of salts of weak acids and weak bases may be either alkaline or acidic, according to which is weaker, or may be nearly neutral (e.g. ammonium acetate).

First consider a salt BA, where HA is a weak acid but BOH a strong base. Then the action $B\cdot + OH' \rightarrow BOH$ does not take place to any perceptible extent, whereas the action $H\cdot + A' \rightarrow HA$ takes place to an extent governed by the equation $\dfrac{[H'][A']}{[HA]} = K_A$, where K_A is the dissociation-constant of the acid. Let the dilution of the salt be V (that is, let one gram-molecule of BA be dissolved in V litres of water), and let a fraction x of the A' ions be combined with hydrogen ions from the water to form undissociated HA. Then $[A'] = \dfrac{1-x}{V}$ and $[HA] = \dfrac{x}{V}$. Now the concentration of hydrogen and hydroxyl ions originally present in the water is negligible in comparison with the concentration of the ions of the added salt, but for every hydrogen ion provided by the water to combine with an A' ion, a free hydroxyl ion must be left in solution. Therefore $[OH'] = [HA] = \dfrac{x}{V}$. Remembering that in all aqueous solutions $[H'][OH'] = K_W$, we have that $\dfrac{x^2}{V(1-x)} = \dfrac{K_W}{K_A}$. The fraction x is called the *degree of hydrolysis*, and when it is small (as it often is) we may write as an approximation $\dfrac{x^2}{V} = \dfrac{K_W}{K_A}$ or $x = \sqrt{\dfrac{K_W \cdot V}{K_A}}$. This makes $[H']$ equal to $\sqrt{K_A \cdot K_W \cdot V}$. By similar reasoning the degree of hydrolysis (when small) of the salt of a strong acid and weak base (dissociation-constant K_B) can be shown to be $\sqrt{\dfrac{K_W \cdot V}{K_B}}$, and the hydrogen ion concentration is then $\sqrt{\dfrac{K_W}{K_B \cdot V}}$.

These equations:

$$[H^{\cdot}]=\sqrt{K_A.K_W.V} \quad \text{and} \quad [H^{\cdot}]=\sqrt{\frac{K_W}{K_B.V}},$$

can be used only for dilute solutions and low degrees of hydrolysis, but are of great practical importance. The student should note (1) that the degree of hydrolysis and the hydrogen ion concentration are both independent of the nature of the strong constituent; (2) that the dilution appears as a square root, so that the hydrogen ion concentration varies comparatively slowly with changes in concentration. As an illustration we may calculate the degree of hydrolysis and hydrogen ion concentration of solutions of sodium acetate at 25° and various dilutions.

The dissociation-constant K_A of acetic acid at this temperature is 1.8×10^{-5} and $K_W=1 \times 10^{-14}$. In M/10 solution, therefore,

$$x=\sqrt{\frac{10 \times 10^{-14}}{1.8 \times 10^{-5}}}=7 \times 10^{-5}, \text{ or } 0.007 \text{ per cent,}$$

while $\quad [H^{\cdot}]=\sqrt{1.8 \times 10^{-5} \times 10^{-14} \times 10}=1.3 \times 10^{-9}.$

Similar calculations at other dilutions give the following results:

V	10	100	1,000	10,000
x (per cent)	0.007	0.02	0.07	0.2
$[H^{\cdot}]$	1.3×10^{-9}	4.2×10^{-9}	1.3×10^{-8}	4.2×10^{-8}

These figures show how small is the hydrolysis of such a salt, even at high dilution. Nevertheless the alkalinity of sodium acetate solutions can easily be detected by *indicators*, whose behaviour in solutions of varying hydrogen ion concentration must now be considered.

Indicators.—Hydrogen ion indicators are substances whose colour changes rapidly with change of hydrogen ion concentration of the solution in which they are dissolved. It was early recognized that this change of colour was due to a change of ionization, and it is indeed found that all indicators of this class are either weak acids or weak bases. We may suppose that the colour of the ions differs from the colour of the undissociated molecule: the more modern idea is that the molecule exists in two tautomeric forms, one of which is fully dissociated while the other is incapable of dissociation, the undissociated form and the ions having different colours.

Form A	$\rightleftharpoons$	Form B	$\rightleftharpoons$	Ions
incapable of dissociation		*fully dissociated*		*coloured differently from A*
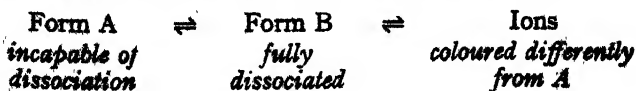
Without discussing this suggestion we shall represent the ionization of an acid indicator in the simplest possible way:

$$HIn \rightleftharpoons H^{\cdot} + In',$$

supposing HIn, in whatever form it may exist, to be differently coloured from In'. The hydrogen ion is, of cou , colourless.

Let K_I be the dissociation-constant of the indicator, which is a weak acid. Then $\dfrac{[H^{\cdot}][In']}{[HIn]} = K_I$. Now as an approximation it is reasonable to suppose that the indicator will appear to change most strikingly in colour when the differently coloured forms HIn and In' are present in equal concentration. At this point $[In'] = [HIn]$ or $[H^{\cdot}] = K_I$. This relation is of fundamental importance in the study of indicators. It tells us that an indicator will change colour when the hydrogen ion concentration of the solution is approximately equal to its own dissociation-constant. The magnitude of the dissociation-constant is therefore the most important property of the indicator. A few values for common indicators are given in the table:

Indicator	Dissociation-Constant
Methyl orange	4×10^{-4}
Methyl red	10^{-5}
Bromthymol blue	10^{-7}
Phenolphthalein	10^{-9}
Thymolphthalein	10^{-10}

Titration.—When a titration is to be carried out an indicator is required which will change colour when equivalent quantities of acid and base have been mixed. If both acid and base are strong the resulting salt solution will be exactly neutral, that is to say, its hydrogen ion and hydroxyl ion concentrations will both be equal to 10^{-7}. But if either acid or base be weak the resulting salt will be hydrolysed in solution, and even though the degree of hydrolysis may be small, yet the hydrogen ion concentration may differ considerably from 10^{-7}; see for example the table showing the hydrogen ion concentrations of sodium acetate solutions. Consequently bromthymol blue must be used only for strong acids and bases; for other titrations the hydrogen ion concentration of the salt solution at the equivalence point must be calculated and an indicator selected with a dissociation-constant approximately equal to this value. An example will make this clear. When equal volumes of M/5 acetic acid and sodium hydroxide have been mixed, the resulting solution is M/10 in sodium acetate. We have already (p. 205) calculated the hydrogen ion concentration of this solution to be $1 \cdot 3 \times 10^{-9}$: phenolphthalein changes colour very near

this concentration and this is the indicator that must be used.   The hydrogen ion concentration is so slightly affected by the dilution of the sodium acetate that we shall always be correct in selecting this indicator for the titration of sodium hydroxide (or any other strong
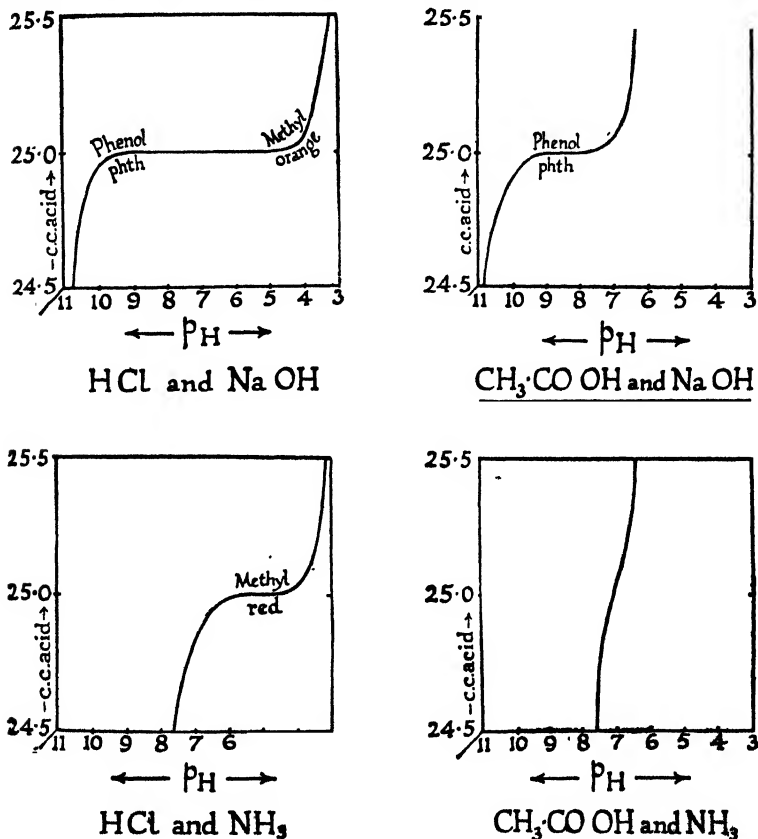
FIG. 68.   TITRATION CURVES

base) with acetic acid (and most other weak acids), but at very great dilutions the determination of the exact end-point will be difficult whatever indicator is used.

The changes that take place in the hydrogen ion concentration of a solution near the end-point of a titration can be brought out very clearly by a graphical method (Fig. 68).   In any titration it

is essential that the hydrogen ion concentration should at the end-point change very rapidly as the acid is added. If a small addition of acid does not bring about a considerable change in the hydrogen ion concentration, the indicator will alter in colour gradually instead of showing a sharp change on the addition of a single drop. The diagrams show the changes that take place in the hydrogen ion concentration near the equivalence point (2 per cent on either side) when various M/10 acids are added to 25 c.c. of various M/10 bases. A sharp change in the colour of the indicator takes place only on the flat parts of the curve. From these examples the following rules for titration can be drawn:

(i) *Strong acids and strong bases:* any indicator from 10^{-9} to 10^{-5}.
(ii) *Strong acids and weak bases:* methyl red or methyl orange.
(iii) *Weak acids and strong bases:* phenolphthalein or (for very weak acids) thymolphthalein.
(iv) *Weak acids and weak bases:* this titration cannot be successfully carried out with any indicator.

Buffer Solutions.—If to the solution of a hydrolysed salt one of the products of hydrolysis is added (e.g. acetic acid to sodium acetate), the hydrolysis is repressed in accordance with the law of mass-action. Such mixed solutions have the useful property of showing very slight changes in hydrogen ion concentration on dilution or on the addition of small quantities of strong acids or bases. For this reason they are termed ' buffer solutions,' and are used when it is desired to keep the hydrogen ion concentration at a fixed value. They are much more suitable for this purpose than very dilute solutions of strong acids or bases, which are sensitive to the smallest traces of impurity derived from dust or the vessel in which they are contained. The mode of action of such a buffer solution as a mixture of sodium acetate and acetic acid is not difficult to understand. If a little of a strong acid like hydrochloric acid is added to it, the hydrogen ions of the added acid are absorbed by the acetate ions to produce more acetic acid, and the dissociation of this substance is so slight that a small increase in its concentration has no great effect on the hydrogen ion concentration of the solution. If, on the other hand, caustic soda is added, the hydroxyl ions react with hydrogen ions from the acetic acid, leaving an increased concentration of acetate ions in solution. The weak acids principally used in the preparation of buffer solutions are citric, boric, acetic, and phosphoric.

A set of such solutions can be made up with standard hydrogen ion concentrations (e.g. 10^{-4}, 10^{-5}, 10^{-6}, etc.), and if a small quantity of the same indicator is added to each, the range of the colour change can be effectively demonstrated.

Mixed Indicators.—*In recent years much progress has been made in the preparation of mixed indicators, which show a series of colour changes over a large range of hydrogen ion concentration,* or alternatively show a sharper change at a given hydrogen ion concentration than a single substance can do. Thus SMITH recommends a mixture of methyl orange, methyl red, bromo-thymol blue, and phenolphthalein, which has the following colours:

p_H.	3	4	5	6	7	8	9	10	11
Colour	Red	Red-orange	Orange	Yellow	Yellowish-green	Greenish-blue	Blue	Violet	Reddish violet

Such mixtures are much used in applied chemistry for the rapid determination of hydrogen ion concentrations. A mixture of methyl orange with a blue dye unaffected by changes of p_H ('screened' methyl orange) has colour changes more obvious than those of the plain indicator.

Measurement of Hydrolysis.—The degree of hydrolysis of a solution, like any other form of chemical equilibrium, cannot be directly measured by chemical analysis, since removal of any one of the reactants or products disturbs the equilibrium. From what has already been said it will readily be understood that the measurement of hydrolysis really amounts to the measurement of hydrogen ion concentration; for the degree of hydrolysis x, the dilution V of the salt, and the hydrogen ion concentration are connected by the simple relation $x=[H^{\cdot}]V$ or $x=[OH']V=\dfrac{K_W.V}{[H^{\cdot}]}$, according to whether the hydrolysed solution is acid or alkaline. Some account may now be given of the methods employed.

1. *The Indicator Method.*—The hydrogen ion concentration of the solution is estimated by observing the tint which a suitable indicator takes up when dissolved in it, or a buffer solution is prepared in which the indicator has the same tint and whose hydrogen ion concentration can be calculated. Owing to the difficulty of exactly matching colours by eye the method is not an accurate one, but various colorimetric devices are available and are of some assistance. The effect that salts have on the colours of some indicators is also a source of inaccuracy.

2. *The Conductivity Method.*—This is one of the oldest, and remains one of the best, methods of measuring hydrolysis; in its improved form it is due to BREDIG. It can, however, yield useful results only with salts whose solutions show considerable hydrolysis, say of the order of 1 per cent or more, and has therefore been chiefly applied to the salts of organic bases, which frequently have very low dissociation-constants.

Consider a solution of aniline hydrochloride, $C_6H_5.NH_2.HCl$. This salt yields the ions $C_6H_5.NH_3^{\cdot}$ ('anilinium') and Cl', and on account of the weakness of aniline as a base, hydrolysis takes place and the solution has a pronounced acid reaction. The dissociation constant for aniline is expressed as

$$\frac{[An^{\cdot}]\,[OH']}{[An]} = K_B.$$
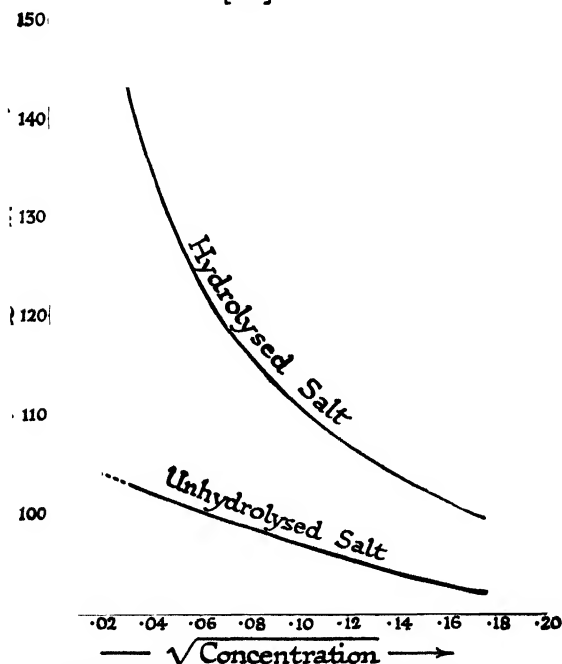
FIG. 69. CONDUCTIVITY OF ANILINE HYDROCHLORIDE SOLUTIONS

If x is the degree of hydrolysis of the hydrochloride at a dilution V, the concentration of the various ions is:

$$[An^{\cdot}] = \frac{\text{I}-x}{V}. \qquad [Cl'] = \frac{\text{I}}{V}. \qquad [H^{\cdot}] = \frac{x}{V}$$

and the equivalent conductivity at this dilution will be:

$$\lambda_V = (\text{I}-x)\mu_{An^{\cdot}} + x.\mu_{H^{\cdot}} + \mu_{Cl'},$$

where μ represents the mobility of the ion at this dilution. Since the hydrogen ion moves very much faster than the anilinium ion that it partially replaces, the equivalent conductivity of aniline hydrochloride solutions rise abnormally rapidly with dilution.

It is possible from the observed values of the conductivity to calculate the degree of hydrolysis directly, but it is better to proceed as follows. Add to the solutions enough aniline to repress the hydrolysis to a negligible amount (quite a small concentration is enough) and measure the conductivity again. The ionization of the added aniline is so small that the conductivity of its ions can be entirely neglected and the aniline hydrochloride now behaves as a non-hydrolysed salt, its equivalent conductivity λ_v' being represented by the simple expression $\lambda_v' = \mu_{An^\cdot} + \mu_{Cl'}$. The diagram shows the conductivities of the hydrolysed and unhydrolysed salt plotted against the square root of the equivalent concentration (p. 149); only the latter gives the normal linear plot. The difference between the two equivalent conductivities at any dilution can now be read from the graph, the calculated value being:

$$\lambda_v - \lambda_v' = x(\mu_{H^\cdot} - \mu_{An^\cdot}), \text{ whence } x = \frac{\lambda_v - \lambda_v'}{\mu_{H^\cdot} - \mu_{An^\cdot}}.$$

The values of $\mu_{H^\cdot}$ and $\mu_{An^\cdot}$ are known from separate experiments, and can without serious error be made equal to the mobilities at infinite dilution, so that x can be calculated with considerable accuracy.

3. *The Distribution Method.* — Aniline hydrochloride will continue to serve as an example. If an aqueous solution of this salt be shaken up with benzene some of the aniline will be extracted, but none of the remaining solutes. The distribution ratio of pure aniline between benzene and water may be measured in separate experiments, and it is found that the aniline is unimolecular in both phases. Consequently the concentration of free aniline in the hydrochloride solution can be calculated by analysing the benzene layer at equilibrium and dividing by the distribution ratio.

<u>Benzene Layer</u>

$$C_6H_5 \cdot NH_2$$

$$|C_6H_5 \cdot NH_2 + H_2O$$
$$\Updownarrow$$
$$C_6H_5 \cdot NH_3^\cdot$$
$$+$$
$$OH'$$

<u>Water Layer</u>

Fig. 70. Hydrolysis of Aniline Hydrochloride Solutions (Distribution Method)

The concentration of the other ions can then be worked out by difference, and the dissociation-constant calculated from the equation:

$$K_B = \frac{[An'] [OH']}{[C_6H_5.NH_2]}.$$

Notice that the degree of hydrolysis can no longer be calculated from the hydrogen ion concentration by the simple equation $x=[H^{\cdot}]V$, because aniline has been withdrawn from the solution and the degree of hydrolysis thereby artificially increased. This increase in the natural hydrolysis is in fact one of the experimental advantages of the method.

4. *The Freezing-point Method.*—Hydrolysis a salt increases the number of solute particles. Thus, if BO is a weak base, the salt BA will·be hydrolysed as follows:

$$B^{\cdot}+H_2O \rightleftharpoons BOH+H^{\cdot},$$
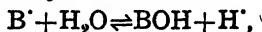
and for each $B^{\cdot}$ ion thus consumed a hydrogen ion and a BOH molecule are produced. The freezing-points of solutions of hydrolysed salts are therefore abnormally low. On account of the variations from ideal behaviour shown by the freezing-points of all electrolytes, most of which are in only moderately good agreement with the freezing-point relation as modified to include dissociated substances, this method is not very precise.

5. *The Catalytic Method.*—The hydrogen and hydroxyl ions are both distinguished by great catalytic activity. The velocity of actions that they catalyse has usually been found to be proportional to the concentration of hydrogen or hydroxyl ion, as the case may be, and the hydrogen ion concentration of the solution of a hydrolysed salt may be estimated by observing the speed of a suitable reaction in it. Such reactions are the saponification of methyl acetate or ethyl acetate (in itself a hydrolysis) whereby an alcohol and acetic acid are produced:

$$CH_3.COOC_2H_5+H_2O \rightleftharpoons CH_3.COOH+C_2H_5OH,$$
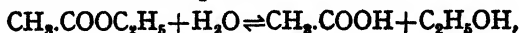
or the decomposition of diazoacetic ester:

$$N_2.CH.COOC_2H_5+H_2O \rightarrow CH_2(OH).COOC_2H_5+N_2 \uparrow.$$
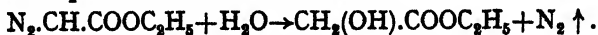
The first can be followed by titrating at intervals the acetic acid produced, the second by gasometry. The inversion of sucrose is also catalysed by hydrogen ions and can be followed with the polarimeter.

In spite of the indirect nature of this method, it has been used with great success on the salts of weak bases (such as urea hydrochloride), which may be 50 per cent or more hydrolysed. For lower degrees of hydrolysis it is not so suitable. By an ingenious modification of the method it is possible to calculate the concentration of hydrogen and hydroxyl ions in pure water by observing the speed of one of these reactions in the pure solvent, and hence to calculate the value of the ionic product of water.

6. *The Electrode Potential Method* of measuring hydrolysis will be explained in Chapter VIII, p. 262.

Homogeneous Catalysis.—We must now turn to the subject of homogeneous catalysis, which is best approached by a consideration of catalysis in solution. Heterogeneous catalysis will be discussed in connection with surface chemistry. It may seem strange to separate what appears to be one subject into two divisions according as the phenomena considered occur in one phase or two. Experience has, however, shown that homogeneous and heterogeneous catalysis are probably phenomena of a fundamentally different kind, and that although certain ideas can usefully be applied to both, yet an artificial simplification of the subject is likely to lead, and indeed more than once has led, to confusion.

Catalysis is an effect by which certain substances called *catalysts* influence the velocity of a chemical reaction but are themselves unchanged in quantity and chemical composition at the end of it. While different authorities use the word in slightly different senses, we shall define it with the help of the following criteria:

(i) A very small quantity of catalyst must be enough to produce a noticeable effect.

(ii) The catalyst must be unchanged in quantity and chemical composition at the end of the reaction.

(iii) The catalyst must not alter the final state of equilibrium, but only the speed with which it is attained. Since the idea of dynamic equilibrium implies equal speeds for the forward and back reactions, it follows that:

(iv) The catalyst influences the speed of the forward and back reactions to the same degree.

When we come to consider the energy relations of chemical change in the next chapter, we shall see that it is impossible that a substance unchanged in quantity and composition at the end of a reaction should have any effect on the equilibrium attained in it. The third criterion is therefore a necessary consequence of the first two, but for the time we shall find it convenient to retain it.[1]

There are innumerable examples to which these criteria can be applied. When potassium iodide is added in small quantity to hydrogen peroxide solutions the peroxide decomposes into water and oxygen, leaving the potassium iodide unchanged. Acetylene combines with water to form acetaldehyde in the presence of mercuric sulphate, but not otherwise: $C_2H_2 + H_2O = CH_3.CHO$. The catalytic activity of hydrogen and hydroxyl ions has already been briefly mentioned, and we may discuss one or two instructive

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[1] To avoid misconception, it should be observed that such influences as heat and light, since they are not material substances, are of course not to be included in the term catalysts.

reactions in which the applicability of the third criterion—unaltered equilibrium—has at one time or another been questioned.

The velocity of saponification of ethyl acetate in dilute hydrochloric acid is directly proportional to the acid concentration, but the equilibrium expression $\dfrac{[CH_3.COOH]\,[C_2H_5OH]}{[CH_3.COOC_2H_5]}$ appears to differ slightly according to the concentration of hydrochloric acid used as catalyst. It has, however, been pointed out that in calculating this expression the concentration of the water, which is present in excess, has been assumed constant, whereas some of it is undoubtedly combined with the hydrochloric acid catalyst; this explains the slight variation in the position of equilibrium with the acid concentration. Again, several reactions are known of which the course, and not merely the velocity, can be altered by the use of suitable catalysts. Thus, when toluene is acted on by chlorine in the absence of a catalyst, benzyl chloride is produced ($C_6H_5.CH_2Cl$), but in the presence of such substances as iron or iodine, the product is a mixture of ortho- and para-chlorotoluenes ($CH_3.C_6H_4.Cl$). It is generally supposed that in such reactions true equilibrium is not reached, and that one at least of the alternative products is metastable. Instances are known in which a reaction takes a different course in different solvents, e.g. in liquid ammonia, but not in water, calcium nitrate and sodium chloride will produce a precipitate of calcium chloride. It is, however, obvious that a solvent, which must be present in comparatively large proportions, cannot possibly be brought into line with the usual definition of a catalyst.

The Intermediate Compound Theory.—Most of the known examples of homogeneous catalysis may be accounted for by supposing (a) that the catalyst forms an intermediate compound with one of the reactants, (b) that this intermediate compound reacts more rapidly than the original substance, and (c) that the catalyst is recovered in the change (the ' intermediate compound theory '). This explains the observed fact that the reaction velocity is usually proportional to the concentration of catalyst, and the intermediate compound in some catalysed reactions has been isolated. Thus Friedel and Crafts' reaction between aromatic hydrocarbons and organic halides takes place when the system includes anhydrous aluminium chloride:

$$C_6H_6 + C_2H_5Cl[+AlCl_3] = C_6H_5.C_2H_5 + HCl[+AlCl_3],$$
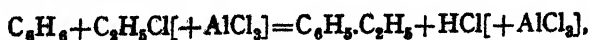
and compounds between the alkyl halides and aluminium chloride ?ve been isolated. The yield is much reduced by the presence even ?quite small amounts of water, presumably because water reacts ?th aluminium chloride and destroys its activity. We shall

revert to this point when we come to *inhibitors*, or negative catalysts.

In some cases the intermediate compound can actually be seen. Hydrogen peroxide solutions are unaffected by either cobalt chloride or sodium potassium tartrate, but addition of both together to the boiling solution causes a bright green compound to be formed, which afterwards decomposes, liberating oxygen and carbon dioxide, and leaving the pink cobalt salt in solution. In this reaction the cobalt ion is the catalyst, since the tartrate is consumed. The view that in catalytic reactions the catalyst undergoes a reversible chemical change is supported by the unusual catalytic activity of compounds of certain metals (such as iron, cobalt, or platinum) which exhibit variable valency, but there is no reason to suppose that the formation of intermediate compounds is not equally the explanation of the catalytic activity of the hydrogen ion. It has already been emphasized that the proton has the power of attaching itself to neutral molecules: $H_3O^{\cdot}+A \rightleftharpoons AH^{\cdot}+H_2O$. In aqueous solution the catalytic power is somewhat blunted by the water molecules that are almost certainly associated with it, and an enormous increase in the velocity of reactions catalysed by hydrogen ions is observed when absolute alcohol is substituted for water as the solvent. The addition of traces of water to the alcoholic solution immediately reduces the catalytic activity of the hydrogen ion, and it has also been observed that the addition of traces of water to a solution of hydrogen chloride in ethyl alcohol causes a large decrease in the electrical conductivity.

Intensive Drying.—Special considerations apply to the catalytic activity of water itself, which appears to be unique in influencing not only chemical changes but physical changes as well. While it had been observed as early as the eighteenth century that dry carbon monoxide would not burn, the principal investigations of water-catalysis are due to BAKER. We shall first consider the effect on the physical properties of substances of the exclusion of all traces of water. Water is present in all chemical systems unless very rigorous steps are taken to exclude it. Modern technique is based chiefly on heating the glass apparatus nearly to fusion in a vacuum and on the use of phosphorus pentoxide over periods of several years as a desiccating agent.

Some of Baker's most remarkable results are concerned with the effect of intense drying on the melting- and boiling-points of pure compounds. The liquids were sealed up in distilling-flasks for nine or ten years in contact with phosphorus pentoxide, which was sometimes in the liquid, sometimes out of it. At the end of this period the tip of the side-tube was broken under dry mercury and the boiling-point determined by thermometers in the liquid

and in the vapour. All the liquids showed a marked increase in boiling-point. Mercury boiled at 420° instead of 358°, ethyl ether at 83° instead of 35°, benzene at 106° instead of 80°. Although precautions had been taken to avoid superheating the liquids, the two thermometers showed different temperatur

On exposure to the air the different liquids reverted to their normal properties with very different speeds—the alcohols very quickly, ether in a day or two, benzene not for several days. The new properties of the benzene were indeed astonic ngly persistent; it was actually found that it did not boil when a lower layer of water was boiled through it.

Other physical measurements were carried ut on the dried liquids, with remarkable results, for though the surface tension and vapour density were found to have suffered notable changes, the density of the liquid appeared to be the same as before. The boiling-point, surface tension, and vapour-density results all indicate that the effect of intensive drying has been to increase the degree of association of the liquid, and if this is the explanation it is very odd that the density of the liquid should remain unchanged. It must be remembered that the validity of Baker's results is not yet certainly established, and that many attacks have been made on them. LENHER attributed the alleged rise in boiling-points to superheating, and by adopting Baker's method of heating in a bath was able to heat benzene to 106° without boiling it if the liquid was first freed from dust (but not from water). In another of Baker's experiments two platinum plates at a potential difference of 400 volts were placed in benzene and a rise in boiling-point observed; but SMITS was not able to confirm this result. Some workers have confirmed the rise in boiling-point on intensive drying, others have denied it. The technique is difficult, and we may have to wait some years before the question is definitely settled. If Baker's results are finally confirmed they are likely to have much effect on the development of chemical theory. Nevertheless, the tendency of the most recent investigators is to attribute the apparent rise in the boiling-points of intensively dried liquids to superheating.

While some of these physical experiments are still open to question, the chemical activity of water as a catalyst is firmly established. In the absence of water, sodium or potassium can be distilled in oxygen without combination, and sodium, magnesium, or zinc can be raised to a red heat in chlorine. A mixture of hydrogen and oxygen can be heated to 1,000° C. without explosion. Dry ammonium chloride volatilizes extremely slowly on heating, although the vapour is completely dissociated. There is, however, one important feature of water catalysis that must

be emphasized, namely that it is restricted to heterogeneous or photochemical reactions. There are a few homogeneous reactions that take a different, and sometimes a more rapid course, in the presence of water, e.g. the combustion of carbon monoxide, which in the presence of steam follows the course:

$$CO + H_2O = CO_2 + H_2. \qquad 2H_2 + O_2 = 2H_2O.$$

In general, however, reactions catalysed by water are either explosive or heterogeneous, and there is no good evidence that a homogeneous reaction (excluding photochemical changes) that proceeds at a measurable rate in the presence of water has ever been stopped by intensive drying. Intensive drying in heterogeneous systems will be further discussed in Chapter IX.

Negative Catalysis.—Catalysts may sometimes retard reaction velocity. Such *negative catalysts* are sometimes called *inhibitors*. Here again we must distinguish between homogeneous and heterogeneous systems. In homogeneous systems the inhibitor probably combines either with one of the reactants or with some positive catalyst that may be present (compare the effect of water on Friedel and Crafts' reaction, p. 214). Just as in positive catalysis, a minute amount of the active substance can produce enormous effects. The rate at which sodium sulphite solutions absorb oxygen from the air can be reduced by 99 per cent by the addition of 0·000005 molar brucine hydrochloride. Similarly the oxidation of benzaldehyde is much retarded by a trace of sulphur. The chain-reaction theory has been used to account for negative catalysis. Thus the reaction between hydrogen and chlorine in sunlight is supposed to take place when a hydrogen or chlorine molecule is split into atoms; each atom then starts a reaction chain which continues until two atoms of the same element recombine:

$$Cl_2 = 2Cl. \qquad Cl + H_2 = HCl + H. \qquad H + Cl_2 = HCl + Cl, \text{ etc.}$$
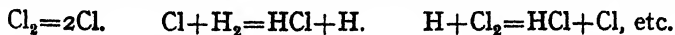
The retarding effect of oxygen is attributed to its power of interfering with the propagation of the chains.

An interesting example of negative catalysis is afforded by the ' anti-knock ' compounds, such as lead tetraethyl, $Pb(C_2H_5)_4$, that are nowadays frequently added to petrol. ' Knocking ' is believed to be due to the decomposition of certain unstable peroxides formed from the hydrocarbons of the petrol and oxygen from the air. These peroxides start reaction chains which result in the formation of more peroxide, and the anti-knock compound is supposed to bring these reaction chains to an end by itself reacting with the peroxides.

Promoter Action.—Catalysis of the second degree is also known, in which a second substance, called a *promoter*, increases the activity of the catalyst. It is frequently found that a mixture of two

substances is a more effective catalyst than either separately: thus traces of iron usually increase the catalytic activity of copper and cobalt salts. The intermediate compound theory is probably the best available explanation of these phenomena, but the student should be on his guard against 'explanations'—of which the literature of chemistry contains a great number—in which without evidence the formation of unknown complexes is assumed. Such theories must remain provisional until it can be shown that such complexes can be formed under the conditions of the experiment, that they do catalyse the reaction, and that they are unstable.

SUGGESTED FOR FURTHER READING

KOLTHOFF and SANDELL: *Textbook of Quantitative Inorganic Analysis* (1952).

BELL: *Acids and Bases* (1952).
'The Use of the Terms "Acid" and "Base," *Chem. Soc. Quart. Rev.*, *1*.

CHAPTER VII

CHEMICAL ENERGY

Thermodynamics—Objects of chemical thermodynamics—The mechanical
equivalent of heat—Energy of reaction—Calorimetry—The adiabatic
calorimeter—Heats of combustion—Vacuum calorimeters—Hess's law—
Heats of formation—Chemical affinity—The principle of maximum work—
Work and free energy—Notation—Carnot's theorem and the second law
of thermodynamics—The Gibbs-Helmholtz equation—Free energy and
chemical change—The law of mass-action and the free energy of chemical
reaction—The effect of change of temperature on chemical equilibrium—
Systems at constant pressure—The free energy of formation—The equili-
brium constants K_p and K_c—The kinetic theory and the isochore—Energy
of activation—Explosive reactions—Applications of the isochore—Kirch-
hoff's equation and the Nernst heat theorem—Applications of the Nernst
heat theorem

Thermodynamics.—We have hitherto based our treatment of
chemistry almost entirely on the molecular theory, and with the
help of the kinetic view of matter have been able to begin the
discussion of the equilibrium between different kinds of matter.
While this method is instructive and illuminating, it is frequently
marred by lack of rigorous treatment and proof. This shortcoming
is mainly due to the prominence necessarily accorded to the question
of chemical mechanisms. In so far as we are still uncertain or
ignorant of many of these, laws deduced from molecular-kinetic
postulates alone will forfeit a certain degree of authority. It is
therefore fortunate that there is another way of approach—the
thermodynamic. Thermodynamics is a science that deals with the
energy effects accompanying chemical and physical changes by
methods which are quite independent of any theories as to the con-
stitution of matter, and therefore of chemical mechanism. Just as
the science of exact chemistry dates from the discovery of the Law
of the Conservation of Mass, so does the science of thermodynamics
owe its progress as an exact study to the great discovery of the *Law
of the Conservation of Energy* by MAYER and JOULE.

Objects of Chemical Thermodynamics.—The idea of energy is
less readily grasped by the mind than the idea of matter, and
since the methods of thermodynamics tend to be highly abstract
most beginners find it a difficult subject. The majority of kinetic
explanations can be assisted by mental images or models, but this
is not true of thermodynamical reasoning, which indeed frequently
abandons even the idea of energy to discuss properties still harder

to associate with the world of the senses.   These difficulties should not deter a beginner from the study of the subject, but before he begins it he should understand exactly what it has to offer him and what the problems are which he is attempting to solve with its aid.

The history of chemistry in the last century and a half has shown an increasing preoccupation with the reasons for chemical change rather than with the collection of new facts.   Whereas the early triumphs of the chemist were concerned with the preparation of a new substance or the discovery of a new reaction, modern research has attempted to discover new principles by which whole series of such observations can be explained.   The doctrines of the indestructibility of matter and of the atomic theory marked great steps forward, but since there was no information—and only a few inaccurate hypotheses—about the nature of atoms, it was not possible to explain, but merely to observe, their behaviour.   By studying the energy relations of chemical change it is possible to understand much that must otherwise remain obscure, and in particular to form some ideas of the great problem of chemical affinity: Why will substance A react with substance B but not with substance C?   In the following pages we shall examine as simply as possible the application of a few fundamental thermodynamical principles to chemistry, but the student must bear in mind that a thorough grasp of thermodynamics can only be acquired by a preliminary study of the simpler systems in which only one component is present.

The Mechanical Equivalent of Heat.—It was a chemical observation that first led to the calculation of the mechanical equivalent of heat.   Mayer, a young German doctor with very little training, was sent on a voyage to Java, and in the course of his duties had occasion to bleed the crew soon after they reached the tropics. He was struck with the unusually bright red tint of their blood, which indicated a decrease in the consumption of oxygen, and asked himself why a man should require a smaller daily amount of oxygen in the tropics than in Germany.   This led him to consider the energy released when food was consumed in the body, and in 1842 he was able to make the first estimate of the mechanical equivalent of heat.   Joule's later and more accurate determination by the physical method is familiar to all students of physics.

Energy of Reaction.—The most obvious sign that energy is involved in chemical change lies in the great quantities of heat liberated in certain common reactions.   When a single gram of hydrogen is burned it liberates more than 30,000 calories—enough to raise about half a pint of water from room temperature to the boiling-point.   When a mixture of aluminium powder and iron

oxide is ignited the temperature rises above the melting-point of most of the common metals: a fact that is made use of in welding steel rails together. Such reactions are called *exothermic*. The absorption of heat when a reaction takes place is less common and the quantity of heat involved is usually much smaller, but such reactions are well known: they are called *endothermic*. The reaction between thionyl chloride and glacial acetic acid is an example that can easily be demonstrated. When seen from a theoretical rather than a practical point of view endothermic reactions are only of conventional significance. Fundamentally all chemical compounds must be referred to the elements which compose them, but so long as we were ignorant of the energy liberated in such reactions as $2O=O_2$, or $2H=H_2$, heats of formation of compounds were of necessity referred not to atoms but to what are essentially very stable compounds of atoms, such as O_2 or H_2. From the two thermal equations

$$2O = O_2, \text{ 117 Cal. liberated,}$$
$$3O_2 = 2O_3, \text{ 68 Cal. absorbed,}$$
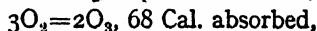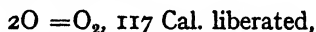
we may, with the aid of the law of conservation of energy, deduce the true heat of formation of ozone, from atoms:

$$3O = O_3, \text{ 141·5 Cal. liberated.}$$
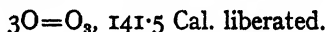
The endothermicity of ozone, although of the first importance in assessing its stability in relation to ordinary (molecular) oxygen, reduces in fact to the statement that the heat liberated per oxygen atom combined is somewhat less for ozone than for ordinary oxygen. When formed from atoms all chemical compounds are exothermic, usually in a very high degree.

Calorimetry.—The heat of reaction can be measured in some form of calorimeter. Unfortunately the sign convention differs with different authors. A chemist, whose science was applied to the study of fuels before the birth of thermodynamics, is naturally loath to abandon the long-established tradition that heat liberated or work done is in a sense profit, and therefore to be reckoned positive. A minor advantage of this chemical convention is that since most chemical reactions are exothermic, only a few (negative) signs need be used or printed. However, this convention has proved confusing and unworkable in thermodynamics, students of which now almost universally adopt the so-called ' acquisitive ' convention: attention is focused on the system under consideration rather than on its surroundings; quantities increasing in magnitude in the system are said to undergo a positive change, and conversely. In the paragraphs which follow on thermodynamics we shall adopt this convention, while retaining the chemical tradition in definitions

of heat of formation, combustion, etc. When the heat change is written with the equation it denotes the heat given out (or absorbed) when one gram-molecule (or the quantity represented in the equation) of the reactants combines with the formation of the products shown. Since heat is involved in the change from one phase to another, it must be stated in the equation whether the reactants and products were in the solid (s), liquid (l), or gaseous (g) state. Standard pressure is assumed unless the contrary is stated. Since the heat of reaction depends on the temperature of the reactants before and the products after the change, this temperature must also be stated, and finally, if the figures refer to a reaction at constant volume, and not, as is more usual, at constant pressure, a note to this effect must be made. The equation

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l) + 68,290 \text{ calories (at } 25°)$$
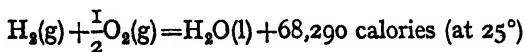
means that at 25° when 2 gm. of hydrogen react with 16 gm. of oxygen, both at a pressure of 760 mm. of mercury, to produce liquid water, the heat given out amounts to 68,290 calories.

In the practical measurement of the heat of reaction special difficulties are encountered which are usually absent from simple physical determinations. The reactions are sometimes very slow, and sometimes do not go to completion, or there may be side-reactions that cannot be eliminated. Sometimes the reactants or products are chemically active, when specially resistant calorimeters have to be used, or they may develop enormous pressures inside closed apparatus. We cannot discuss these special cases, but may mention one or two types of calorimeter in which some of the difficulties have been overcome.

The Adiabatic Calorimeter.—The greatest inaccuracy is due to loss of heat from the calorimeter during the progress of the reaction. This can be reduced by keeping the surroundings of the calorimeter at the same temperature as the instrument itself. The *adiabatic calorimeter*, as it is called, is an invention of RICHARDS. The environment may be heated electrically, or use may be made of the heat liberated when acids neutralize bases. In the *submarine calorimeter* the instrument is entirely immersed in oil or water, whose temperature is continuously varied. The temperature inside the calorimeter and in the bath is read every few seconds with thermometers or thermocouples, and the heating of the bath regulated accordingly. In a further development of the apparatus the heating of the bath is automatically regulated by the difference in reading between two such thermocouples. The temperatures of the calorimeter and of the bath are therefore always equal and no heat losses can take place.

In order to calculate the quantity of heat evolved in the reaction from the rise in temperature which takes place, the thermal capacity of the system must be known, but it is usually simpler to include an electric heater in the calorimeter and to see how much heat must be supplied to the products to raise their temperature through the observed interval. If the two experiments are done under
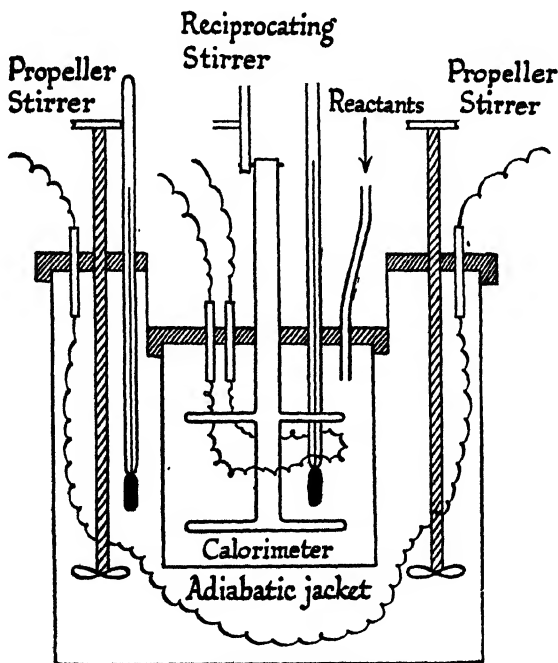
FIG. 71. ADIABATIC CALORIMETER

exactly similar conditions, there is then no necessity to apply any correction for the thermal capacity of the calorimeter.

Heats of Combustion.—The heat of combustion is the heat of reaction which is most frequently determined, and for reasons which will shortly be clear it is one of the most useful quantities for calculation. Combustion is one of the few reactions of organic compounds which proceed to a definite conclusion in a reasonable time: most organic substances can be completely oxidized by oxygen under pressure. Since a considerable pressure is required before the ignition and is developed after it, the bomb calorimeter

*H

originally devised by BERTHELOT is used, and since the heat is evolved very rapidly the adiabatic method is out of the question; the calorimeter is immersed in a known weight of water and its rise in temperature is measured. The water itself may, however, be placed in an adiabatic enclosure.

The bomb consists of a steel-walled vessel with a screw top. A known weight of the substance to be investigated is placed on a platinum plate, where it can be ignited by passing a current through a thin iron wire: a correction must be made for the heat liberated by the combustion of the wire. The combustion is carried out in oxygen under pressure. The walls of the bomb must be lined with gold or platinum to avoid the possibility of oxidation.

Vacuum Calorimeters.—While adiabatic calorimetry has made great progress in recent years in the hands of Richards and others, the DEWAR flask is still much used as a calorimeter. This consists simply of a glass vessel with double walls and a high vacuum between them: the low rate of loss of heat from such vessels is well known and is made use of in the 'Thermos.' Open calorimeters are always avoided, on account of the heat losses due to convection-currents and evaporation, and the vessel is therefore fitted with a lid and with a stirrer, since the temperature of an unstirred liquid may be far from uniform.

A rather different type of instrument has been devised for the measurement of the specific heat of gases at low temperatures. A known mass of the gas is enclosed in a small steel vessel with very thin walls, to which it is conducted at a low temperature through a silver capillary tube. The steel vessel is wound on the outside with two separate coils of platinum wire—one to supply a known quantity of heat, the other to function as a resistance thermometer and measure the rise in temperature produced—and is suspended in a high vacuum. With this apparatus EUCKEN was able to measure the specific heat of hydrogen at temperatures as low as 35° Abs.

BUNSEN'S *ice calorimeter* is still occasionally used to measure the heat change in reactions which are either very slow or give out very little heat, but the experimental difficulties are considerable.

Hess's Law.—We may now consider some of the results of these experiments, and shall find it convenient to employ the law, enunciated by HESS, that *the heat evolved in passing from substances A to substances B is independent of the steps in which the transformation is carried out.* Any contrary conclusion would violate the first law of thermodynamics, for we could create energy by carrying out the change with the maximum evolution of heat and reversing

ıt with the expenditure of a less amount. With the help of this principle we can calculate the heat involved in reactions which it would be difficult or impossible to investigate experimentally. Thus the oxidation of carbon in the form of graphite to carbon dioxide could be carried out either directly, or by first converting it to diamond and then oxidizing the diamond. While the experimental measurement of the allotropic change cannot be undertaken, it is possible to measure the heats of combustion of graphite and diamond, the figures under similar conditions being +94,240 and +94,420 calories respectively. The heat involved in the allotropic change is equal to the difference between these results, so that if graphite could be converted to diamond 180 calories of heat per gram-atom would be absorbed.

Heats of Formation.—In this way it is possible to construct a table showing the heat of formation of various substances under standard conditions from their elements. Three principal units are now in common use for the expression of chemical energy.

Compound	Heat of Formation (Cal.)	Reaction (Gaseous reactants at 1 atm. pressure)
H_2O (l)	68·29	$H_2 + \frac{1}{2}O_2$
H_2O (g)	57·75	
H_2S (g)	5·28	$H_2 + S$ (rhombic)
NH_3 (g)	11·0	$\frac{1}{2}N_2 + 1\frac{1}{2}H_2$
NH_3 (l)	15·8	
NH_3 (N. aq.)	19·4	
HCl (g)	22·1	$\frac{1}{2}H_2 + \frac{1}{2}Cl_2$
HCl (N. aq.)	39·2	
HBr (g)	8·7	$\frac{1}{2}H_2 + \frac{1}{2}Br_2$ (liquid)
HI (g)	−5·9	$\frac{1}{2}H_2 + \frac{1}{2}I_2$ (solid)
HI (N. aq.)	13·2	
CO_2 (g)	94·3	C (graphite) + O_2
SO_2 (g)	70·9	S (rhombic) + O_2
CO (g)	26·8	C (graphite) + $\frac{1}{2}O_2$
NO (g)	−21·6	$\frac{1}{2}N_2 + \frac{1}{2}O_2$
NO_2 (g)	−7·9	$\frac{1}{2}N_2 + O_2$
MgO (s)	139·0	Mg (metal) + $\frac{1}{2}O_2$
CaO (s)	151·3	Ca (metal) + $\frac{1}{2}O_2$
ZnO (s)	84·2	Zn (metal) + $\frac{1}{2}O_2$
As_2O_3 (s)	156·1	As (grey) + 1$\frac{1}{2}O_2$
Al_2O_3 (s)	398·5	Al (metal) + 1$\frac{1}{2}O_2$

(g = gas at 1 atm. pressure; l = liquid, s = solid;
N. aq. = normal aqueous solution)

HEATS OF FORMATION (Heat *liberated* reckoned positive)

The *kilo-calorie* (1,000 calories, symbol k. cal. or Cal.) has the longest tradition, but electrical methods of operating calorimeters have steadily encouraged the use of the *kilo-joule* (symbol kj.). This unit is directly connected with fundamental units by its definition as 10^{10} ergs. One kilo-joule equals 0·2386 Cal. The third unit, the *electron-volt* (symbol ev.), has come into use more recently as a convenient unit for expressing true molecular and atomic energies. One electron-volt is the (kinetic) energy acquired by an electron in being accelerated through a field of 1 volt potential difference. If a molecule acquires this amount of energy, then 1 gm.-mol. acquires 23·06 Cal., or very nearly 100 kj. By convention, the *heat of formation* is *the heat liberated when one gram-molecule of the substance is produced from its elements when these are in the physical and chemical condition usual at room temperatures*. Thus the heats of formation of organic compounds containing only carbon, oxygen, and hydrogen are obtained by deducting from the heats of formation of the carbon dioxide and water produced the heat of combustion of the compound. A negative heat of formation indicates that the compound is formed from its elements with absorption of heat, but here again the practice of different authors must be taken into account. The table (p. 225) shows the approximate heat of formation of some well-known substances at room temperature. All the figures refer to one gram-molecule.

Chemical Affinity.—It is obvious from the table that there is a general connection between the avidity with which certain elements combine and the heat of formation of the compound produced. This is well shown by the halogen acids, whose heats of formation increase in the order of decreasing atomic weight of the halogen; this is certainly the order of their activity towards hydrogen. Indeed, it was at one time supposed that the heat evolved in a reaction was a true measure of the tendency of the reaction to take place—or of its ' chemical affinity '—and to estimate this affinity was the object of many of the early thermochemical investigations. That this view cannot be the true one is shown by the occurrence not only of definitely endothermic reactions but also of balanced actions, for a reaction consumes heat in one direction if it liberates it in the other. The further suggestion was at one time made that affinity might be measured by the velocity of chemical change, but this view is equally untenable. It can scarcely be denied that oxygen and hydrogen have great affinity for one another, yet a mixture of these gases may be kept indefinitely in the absence of catalysts without giving any sign of reaction. The greatest claim which thermodynamics has on the attention of chemists is that it can provide a partial answer to this question. One might expect that the law of mass-action or some extension

of it would be of assistance. It is true that if we know the equilibrium-constant of a balanced action it is possible to predict with the help of this law what direction a reaction will take in a mixture of reactants and products in given proportions. It is, however, impossible to estimate the value of the equilibrium-constant without experiment, but this is what we must try to do. It goes without saying that we can estimate the equilibrium-constant only in terms of some other experimentally determined value—we cannot evolve it out of our inner consciousness. This, however, is a limitation common to the whole of physical science, which is a matter not of creation but of classification. The student may also have observed that the law of mass-action gives us no hint of the effect of temperature on the equilibrium-constant. A qualitative answer to this question is provided by the principle of LE CHATELIER—which we stated without proof—but for the quantitative expression we must fall back on thermodynamics. This more modest inquiry—the effect of temperature—we shall be able to answer completely. The calculation of the magnitude of the equilibrium-constant has as yet been only partially carried out, and many uncertainties are still involved in the process. Here we shall be able to do no more than to indicate the direction from which the complete solution will probably come.

The Principle of Maximum Work.—It will first be necessary to state more precisely what we mean by affinity. The affinity of a chemical reaction is the tendency which the reaction has to take place, in the sense that reactions with positive affinity can take place (but may not do so in the absence of suitable catalysts), while reactions with negative affinity cannot in any circumstances take place, and reactions with zero affinity have reached equilibrium. As a measure of the affinity of a reaction we shall take the maximum work which the reacting system can be made to perform. It can be demonstrated by the *principle of maximum entropy* that the only spontaneously occurring processes—that is, the only processes with positive affinity—are those from which work can be obtained. If the student's knowledge of physics does not carry him so far as the conception of entropy he must be content with the information that the principle here enunciated is a consequence of the second law of thermodynamics, which is independent of the molecular theory of matter. We may, however, give a mechanical explanation of what is meant by *maximum work*. It is obvious that while the same mechanical process, if carried out in different ways, must liberate the same amount of energy, the proportion of this energy which appears as external work performed by the system is variable. If a weight is allowed to fall freely through a given distance, the whole of the kinetic energy at the bottom, which is

equal to the potential energy at the top, is dissipated in heat and sound. If, however, before releasing the weight we attach it by a cord passing over a frictionless pulley to a very slightly smaller weight, then the system, when released, will move slowly, the falling weight will have a negligible kinetic energy on reaching the ground, and nearly the whole of the energy will have been retained in the form of potential energy of the weight which has been raised. The process has then been carried out with the performance of the maximum work and with the dissipation of the minimum amount of energy as heat. This can be done only if the system is acted on at any moment by the smallest force which will move it at all, so small in fact that any reduction in it would cause the system to move in the opposite direction. When the process has been carried out under such conditions it is called a *reversible process*, and the work which can be got from a process is always a maximum when the process is carried out in a reversible manner. It might be thought that, by demanding reversible processes to give a true measure of affinity, we shall again be concerned with mechanism, and the disadvantages of the purely chemical approach already mentioned. It must, however, be remembered that any mechanism whatsoever, even one entirely impracticable, that is reversible will lead to the same valuation of the affinity as any other. In point of fact a perfectly reversible process is a theoretical figment, and can never be actually realized, but this idealization does not in the least detract from the validity of the thermodynamical predictions. The affinity so determined will still be authentic for an actual, practical, but certainly at least partially irreversible process.

As an example of a chemical process reversibly carried out, we may consider the compression of a mixture of ammonium chloride vapour with its products of dissociation: $NH_4Cl \rightleftharpoons NH_3 + HCl$. If the pressure on the system is gradually raised, we know from Le Chatelier's principle that ammonia and hydrogen chloride will combine; if it is gradually released more ammonium chloride dissociates. If properly carried out, the process involves no dissipation of energy.

Certain types of galvanic cell are excellent examples of reversible processes; they will be considered in the next chapter.

Work and Free Energy.—The term *work* is properly used when we think of the surroundings of a system and the effect it has upon them. From the thermodynamical standpoint, however, attention is focused on the *loss* of energy by the system in performing external work. The thermodynamic quantity corresponding with work, termed the *free energy* (of the system), was first introduced by HELMHOLTZ, and so named by him. He regarded a system as holding a certain store of free energy F', which may, under suitable

conditions, be diminished by its issue and realization as external work w, of equal magnitude but opposite sign to the change of free energy, or be increased by the performance of work on the system

$$w = -\Delta F'.$$

The balance, making up the *total energy* of the system U', he called the *bound energy* Q'; it is realizable externally only as heat, and may be increased by adding heat to the system. It is simple to calculate the change of free energy of 1 gm.-mol. of a perfect gas, when a change is made in the pressure, at constant temperature. Since $pV = RT = \text{constant}$,

$$-\mathrm{d}F' = p\,\mathrm{d}V = -V\mathrm{d}p = -RT\ \mathrm{d}\log p.$$

Thus for a finite pressure change from p_1 to p_2 we have

$$F_2' - F_1' = RT\ \log (p_2/p_1).$$

That the conception of free energy is broader and more fundamental than that of work appears in many ways, but particularly in the fact that a change of temperature will produce a change of free energy, even when the change is *isosteric*, that is, conducted at constant volume, so that no work terms can arise. The reader should consult a textbook of thermodynamics for a proof of this, as it is outside the scope of this chapter. The relation $w = -\Delta F'$ is therefore valid only for changes conducted at constant temperature, called *isothermal*, and moreover these changes must be ideally reversible. The same conditions apply to the relation of heat q to the bound energy Q', given by the equation

$$q = -\Delta Q'.$$

The application of the idea of free energy is not, of course, limited to the gaseous state, although in that case the calculation of its changes in terms of p, V, and T is often simple. Modern developments in thermodynamics have shown how the absolute magnitudes of quantities, such as free energy, may be evaluated, but it remains customary and convenient to assign arbitrary datum lines to thermodynamic quantities. We take *pure solids, pure liquids,* and *gases at 1 atmosphere pressure* to have *zero free energy*. Free energy reckoned from this zero is often termed the *standard free energy*. When we have to deal with solutions the standard free energy of the solute is reckoned from the datum line of molar concentration $C = 1$. On this convention the ideal gram-molecular free energy of a gas or solute is $RT \log p$ and $RT \log C$ respectively.

Notation.—Our arguments will be largely concerned with *changes* of free energy, and total energy, often written ΔF and ΔU, but to avoid the continual repetition of such rather clumsy symbols we ask the reader to assume that an unprimed simple symbol, such as F or U, means always a finite *change* in the quantity concerned.

On the infrequent occasions when values of these quantities referred to an arbitrary standard state are required we shall use primed symbols, F', U', etc. Thus $F = F_2' - F_1'$.

The reader's attention must be drawn to the prevailing confusion in regard to the symbolization for free energy, to which we shall continue to assign the symbols F and F'; some authors, however, prefer the symbol A, and employ F for an allied quantity (the ' chemical ' free energy G, p. 235).

Carnot's Theorem and the Second Law of Thermodynamics.—The first law of thermodynamics is concerned with the energy of a system as a whole; it states that the sum total of energy of all types is conserved in an isolated system. The province of the second law lies in the limitations governing the interconversion of free and bound energy. CARNOT, before the acceptance of the first law, discussed this question under the guise of the efficiency of a heat engine, which he defined as the ratio w/q, where w is the useful work obtainable by the expenditure of heat q into the engine. His work, although epoch-making when seen in the light of later developments, was obscured by his apparent ignorance of the first law, and by a vague attitude on the meaning of temperature. He was, however, the first to appreciate that an ideal engine is a perfectly reversible machine. KELVIN first gave precision to Carnot's ideas, and showed how to define temperature on the absolute scale which we now use. Carnot's theorem on efficiency could then be quantitatively expressed by the equation

$$w/q = (T_2 - T_1)/T_2$$

where $(T_2 - T_1)$ is the working temperature range on the absolute scale of an ideal, that is perfectly reversible, engine. In differential notation this equation takes the form

$$dw = q\,dT/T,$$

which is an expression of the second law. In modern terminology it may be said to provide the law of the conversion of bound into free energy, and it demonstrates how this conversion is dependent on a difference in temperature. "

The Gibbs-Helmholtz Equation.—In any change, physical or chemical, the net change U in the total energy of the changing system must be, by the law of conservation of energy, the algebraic sum of the changes in bound and free energy, Q and F respectively,

$$U = Q + F.$$

The change U is sometimes termed the change in ' internal ' energy, but this description is ill chosen, and frequently misleading. To clarify the application of this important equation, typical cases for

a system X, operating perfectly reversibly at constant temperature T, are tabulated below.

Change	Q	F	U
(1) Heat q absorbed Work w done by X	q	$-w$	$q-w$
(2) Heat q liberated Work w done on X	$-q$	w	$w-q$
(3) Heat q absorbed Work w done on X	q	w	$q+w$

From the equalities $dw=-dF$, and $q=+Q$ (p. 229), we may transcribe Carnot's relation $dw=qdT/T$ into

$$-dF=+QdT/T$$
$$\text{or} \quad -Q=T(dF/dT).$$

Since $U=Q+F$, we have at once

$$F-U=T(dF/dT).$$

This is the GIBBS-HELMHOLTZ equation in its original form. It may be written in the equivalent, but more compact and useful, form

$$\frac{d(F/T)}{dT}=\frac{-U}{T^2}.$$

By carrying out the differentiation indicated, the second form transforms at once into the first. We shall need the second form in deriving the reaction isochore.

The Gibbs-Helmholtz equation (in either form) relates the change F in free energy and the associated change U in total energy, when the change is accomplished isothermally at temperature T. It is of the first importance to realize that the equation is rigorously applicable to actual, and therefore at most partially reversible, changes. It is no less valid for completely irreversible changes. If an isothermal change is ideally reversible, then the whole change F is realized as (external) work; if the change is not reversible, then only a small part or none of the free energy change will appear as work, but the free energy change will still be precisely that specified in the Gibbs-Helmholtz equation.

Free Energy and Chemical Change.—We may now profitably re-state the principle of maximum work in a more general form. *All systems tend to change spontaneously only in the direction of a decrease in their free energy*; when this has been reduced to a minimum the system ceases to change, and comes into a condition of equilibrium. We connect what has been called the affinity of a reaction directly with the corresponding change of free energy. If we are now asked how this change of free energy, and therefore the affinity,

may be ascertained, we can give the prescription: (1) select a reversible mode for effecting the reaction, (2) measure the work obtained when the reaction proceeds in this mode, and reverse its sign. If the change is effected irreversibly it only means that the work obtained, if any, has no relation to the affinity, but the affinity is still measured by the free energy change, and is a fixed property of the reaction, and in no way dependent on how the reaction is conducted. There may be many routes, reversible and irreversible, by which a system can move from one chemical state to another, but the law of the conservation of energy tells us that whatever the route chosen, the difference of total energy U between the states will be precisely the same. We have met this principle already in Hess's law (p. 224). The same property, of independence of route, is manifested by the free energy F. In the simple example of the change of free energy of a gas with pressure (p. 229), we made the calculation on the assumption that the pressure change took place reversibly, and used the relation $w = -F$. The change of free energy would be exactly the same if we had imagined the expansion to take place suddenly into an evacuated vessel of suitable capacity, but no work would have been gained. In the reversible expansion heat q must be passed into the gas to maintain constant temperature, and this heat is exactly equivalent to the work done by the gas, the total change of energy U being zero. Thus we have $U = -F + Q = 0$, where $w = -F$, and $q = Q$. During the irreversible expansion no heat is supplied, but free energy F is converted into bound energy Q. Again we have $U = -F + Q = 0$. Thus the gaseous system suffers exactly the same changes in its free and bound energy in both types of expansion. It is only when we seek a ready means of evaluating changes in thermodynamic quantities such as F and Q, in terms of p, V, and T, that we must often confine our attention to specified types of route, such as those that are perfectly reversible, but the results so found are universally applicable. It must be noted that both work and heat changes are quantities dependent on the choice of route. Those readers familiar with the more physical aspects of thermodynamics will be aware that it is precisely to circumvent the dependence of heat changes upon route that the function *entropy*, S', is introduced. The bound energy Q' referred to above (p. 229) is expressed as the product TS'. It is probably because thermodynamical arguments must necessarily be more concerned with abstract quantities such as free energy and entropy, than with the more familiar work and heat, that the science seems baffling to the beginner; but unless such a basis is adopted, thermodynamical predictions would be valid only for ideal reversible systems, and could not apply universally to actual, practical reactions.

The Law of Mass-action and the Free Energy of Chemical Reaction.
—Let four perfect gases, B, C, D, and E, which react according to the equation

$$B+C=D+E,$$

be mixed at a suitable temperature T, thereafter maintained constant, and steps be taken to promote the attainment of the equilibrium

$$B+C \rightleftharpoons D+E.$$
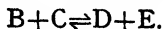
To test whether a true equilibrium has been reached we proceed as follows. If equilibrium has not been attained then some change in the composition of the mixture, say an increase in the pressures p_D and p_E of the resultants D and E, and a decrease in the pressures p_B and p_C of the reactants, will cause a decrease in the free energy of the whole system, and bring it nearer to equilibrium, where the free energy is a minimum. If equilibrium has been reached, then a *small* change of this kind in *either* direction will leave the free energy unchanged, for the condition for a minimum is $dF=0$. Thus equilibrium is reached when for a small change of composition

$$(dF_D+dF_E)-(dF_B+dF_C)=0.$$

We have seen (p. 229) that for a perfect gas $dF=RT$ d log p. Therefore at equilibrium

$$RT(\text{d log } p_D+\text{d log } p_E-\text{d log } p_B-\text{d log } p_C)=0$$

or
$$RT \text{ d log} \frac{p_D p_E}{p_B p_C}=0.$$

Therefore $\dfrac{p_D p_E}{p_B p_C}=$ constant, K (at constant temperature).

If we now have a store of the gases B and C, each at 1 atm. pressure, we may pass 1 gm.-mol. of each of them in successive small amounts through the equilibrium system, and similarly withdraw 1 gm.-mol. of each of D and E, also brought to 1 atm. The free energy change for this operation of the equation $B+C=D+E$ in the forward direction, i.e. *complete* transformation of B and C into D and E, will be due to the stages:

(1) B and C at 1 atm. pressure are brought to the equilibrium pressures p_B and p_C respectively,

(2) D and E at equilibrium pressures p_D and p_E respectively are brought to 1 atm. pressure,

for since B and C react to form D and E under equilibrium conditions, no free energy is lost or gained in the actual chemical change. Hence we see that the free energy change F^o in the forward direction is

$$F^o=RT(\text{log } p_B+\text{log } p_C-\text{log } p_D-\text{log } p_E)=-RT \text{ log } K.$$

This result has brought us to an exact measure of the affinity of the reaction $B+C=D+E$, for by taking the initial and final

pressures as unity, we have eliminated effects due to arbitrary values of the pressures, and placed ourselves in a position to correlate the affinity of one reaction with that of another, when each proceeds at the same temperature. $F°$ is usually termed the *standard free energy of the reaction.*

The Effect of Change of Temperature upon Chemical Equilibrium.—From the results already obtained the problem of how temperature influences chemical equilibrium is easily solved. Let U be the total energy change occurring when 1 gm.-mol. of each of B and C (each initially at unit pressure) is completely converted into 1 gm.-mol. of each of D and E (each finally at unit pressure) by the operation of the equation B+C=D+E in the forward direction. We have seen that the concomitant change in free energy is

$$F° = -RT \log K.$$

From the Gibbs-Helmholtz equation in its compact form we have

$$\frac{\mathrm{d}(-RT \log K)/T}{\mathrm{d}T} = \frac{-U}{T^2} \; ;$$

or, on simplifying:

$$\frac{\mathrm{d} \log K}{\mathrm{d}T} = \frac{U}{RT^2}$$

Now the change in total energy U must be just the energy change registered as heat q_V when the reaction proceeds, necessarily irreversibly, in a calorimeter at constant volume.

Therefore $$\frac{\mathrm{d} \log K}{\mathrm{d}T} = \frac{q_V}{RT^2}.$$

This relation is called the *reaction isochore.* When the chemical sign convention is adopted q_V must be changed to $-q_V$.

If the reaction is exothermic in its forward direction, d log $K/\mathrm{d}T$ is negative, and K decreases with rise of temperature T; that is, the yield of D and E in the equilibrium mixture is lessened. The relation is, of course, the quantitative statement of Le Chatelier's principle in its application to changes of temperature.

Systems at Constant Pressure.—In our derivation of the Gibbs-Helmholtz equation and in the gas reaction B+C=D+E to which it was applied, to illustrate how problems of chemical affinity may be solved, we have tacitly or explicitly assumed that our systems are 'constant volume' systems. In the Gibbs-Helmholtz equation this feature is seen in the meaning of U, and in the conditions of differentiation of the dF/dT term, which should strictly have been written $(\delta F/\delta T)_V$. This condition means that the change of free energy F with temperature T must be measured after steps have been taken ensuring that the pressure on the gaseous system is adjusted to prevent a change of volume as the temperature is

altered. In the chemical equation 'constant volume' means that there is the same number of molecular species on each side. So long as we confine our attention to purely gaseous chemical systems this restriction is not serious, as we can always comply with it by suitable adjustments of pressure and simple calculations. When, however, we deal with systems involving solids and liquids as reactants or resultants such a restriction is prohibitive. In such systems the only practicable condition is constant pressure, usually atmospheric. In the general case, therefore, the *total* free energy change F attending a chemical reaction will consist of two contributions: (1) The change due to the work w involved in the change of volume at constant pressure, given by $p(V_2-V_1)$. This contribution is $-w$. (2) The change associated with the transformations of molecular species, B, C, etc. to D, E., etc., from which the contribution is $F-(-w)=F+w$; it is clearly to this alone that the affinity should be related. We have seen that $F=U-Q$ (p. 230); hence $F+w=(U+w)-Q$. Now it is obvious that when the reaction takes place in a calorimeter at constant pressure the heat change registered must be $q=(U+w)$, for the term w is still involved. Hence the 'chemical' free energy change $F+w=G$, and the ordinary calorimetric measurement $U+w=H$, correspond in the same way as F and U; in particular $G-H=F-U$. Further it may readily be shown that $(\delta G/\delta T)_p=(\delta F/\delta T)_V$. Hence we can write more general forms of the Gibbs-Helmholtz equation thus:

$$G-H=T(\delta G/\delta T)_p : \frac{\delta(G/T)}{\delta T}=\frac{-q_p}{T^2}.$$

These equations really include the form in terms of F and U as a special case, in which $-w=0$. The heats of formation in the table on p. 225 are measurements of H, and not of U. When H is large, its difference from U is commonly small in comparison with its magnitude. The free energies of formation below are likewise values of G, not of F. (Free energy released reckoned *negative*.)

Compound	Free Energy of Formation at 298° K. (Cal.)	Compound	Free Energy of Formation at 298° K. (Cal.)
H_2O (l)	-56.7	CO_2	-94.3
H_2S	-7.84	CO	-32.5
HF	-31.8	NO	$+20.85$
HCl	-22.7	NO_2 (g)	$+12.49$
HBr	-12.5	MgO (s)	-136.4
HI	-2.0	ZnO (s)	-75.7
NH_3	-3.9	As_2O_3 (s)	-137.7

(For reactions, see table, p. 225: all gases at $p=1$ atm.)

FREE ENERGY OF FORMATION

Inspection of this table in conjunction with table on p. 225 for heats of formation discloses that free energies of reaction and heats of reaction commonly have the same sign and comparable magnitudes. We could therefore hold *empirically* that heat of reaction usually gives a rough estimate of the affinity, but that this as a principle is false is well shown by the case of hydrogen iodide, where an endothermic compound is formed spontaneously from its elements owing to the decrease of free energy. It is interesting to contrast nitric oxide NO and nitrogen dioxide NO_2 with carbon monoxide CO and carbon dioxide CO_2. Both the oxides of carbon are thermodynamically stable, there being a substantial decrease of free energy when they are synthesized from graphite and oxygen. On the contrary, neither nitric oxide nor nitrogen dioxide has any thermodynamic sanction to exist at ordinary temperatures: both should change spontaneously into nitrogen and oxygen N_2 and O_2. Thermodynamics, however, affords no information about reaction rates of the changes it predicts. We have in the two oxides of nitrogen an extreme example of sluggish rate of reaction, the sole reason for the practical stability of these oxides.

The Equilibrium Constants K_p and K_c.—We have seen that for the reaction between gases
$$B+C=D+E \tag{1}$$
the total free energy change is a rational measure of the affinity
$$F \text{ (or } G) = -RT \log K = -RT \log \frac{p_D p_E}{p_B p_C}.$$

No distinction need be made here between F and G, for $-w=0$, whether we effect the reaction at constant pressure or constant volume. The equilibrium constant K is usually written K_p, to indicate that it is formed from the partial pressures of the reactants and resultants. Subscripts are often used in thermodynamics to indicate that a certain variable has been kept constant; such, of course, is not the meaning of the subscript p in this case. For the reaction between gases
$$B+C=D \tag{2}$$
$$G = -RT \log K_p = -RT \log \frac{p_D}{p_B p_C},$$
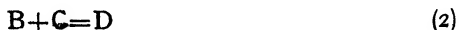
G and not F is the appropriate measure of the affinity. G is the free energy change that would be observed when 1g.-mol. of each of B and C react to give 1g.-mol. of D, all at 1 atm. pressure.

Let us now express p_B, etc., in terms of molecular concentration, C_B, etc., using the relation $p_B = c_B RT$, which holds for a perfect gas.

We see that for reaction (1) $K_p = K_c$, but for reaction (2) $K_p = K_c(RT)$ where K_c is used for the general expression $C_D C_E / C_B C_C$.

If there had been a difference n of molecular species on the two sides of equation (2) we should have found $K_p = K_c(RT)^n$. Now the validity of taking K_p as a true measure of affinity follows upon our choice of the standard gaseous state (p. 229) as one at unit pressure, $p = 1$ (atm.). Had we chosen as the standard state the condition $C = 1$, i.e. 1 gm.-mol. per litre, then K_c would become our measure of affinity. Thus if we wish to adopt K_c to represent affinity, as for example in dealing with solutions, we must agree to take unit *concentration* as the standard state for solutes. When this condition is understood no confusion need arise in the use of K_p and K_c, but they must not be interchanged indiscriminately.

The Kinetic Theory and the Isochore.—The kinetic theory of gases provides us with another valuable method of attack on the problems of chemical change. Two gas molecules can take part in a reaction, if we confine ourselves to homogeneous changes, only when they collide, and from our knowledge of the mean free path—i.e. the mean distance traversed by a gas molecule between collisions, as calculated from independent physical methods —we can calculate the number of such collisions per second in a gram-molecule of the gas under given conditions of temperature and pressure, and hence the maximum possible velocity of the reaction, on the supposition that all such collisions result in chemical change. For reactions taking place at a measurable speed this maximum rate is always greatly in excess of that actually found by experiment. There is another reason why the hypothesis that all collisions are fruitful must be rejected. The temperature-coefficient of the rate of chemical change is usually high; an increase of ten degrees in the temperature usually causes an increase of a hundred per cent or more in the reaction velocity. Now the temperature-coefficient of the number of collisions per second can be calculated without difficulty from the kinetic theory, and is very much less. We are therefore, for these two reasons, forced to conclude that only a small fraction of the total number of collisions that take place result in chemical change. At an early stage of the history of the subject the suggestion was made that only molecules whose combined energy exceeded a certain fixed value would react together. The suggestion has been wholly successful and its consequences must be more closely examined.

Consider a reversible gas reaction, bimolecular in both directions, in which a quantity of heat q_V is absorbed at constant volume, and denote by E_1 the total energy required by two gram-molecules before they can react in one direction, while E_2 is the energy required by two gram-molecules of the product for reaction. Then:

$$E_1 - E_2 = q_V.$$

Now it can be shown by statistical study of the distribution of energy among gas molecules (Chapter II, p. 94) that the fraction of the collisions in which the combined energy of the molecules exceeds E_1 is $e^{-E_1/RT}$, so that the rate k_1 of the forward reaction is:

$$k_1 = \text{constant} \times e^{-E_1/RT},$$

while the rate k_2 of the back reaction is:

$$k_2 = \text{constant} \times e^{-E_2/RT}.$$

The equilibrium-constant k is the ratio of the velocities of the forward and back reactions (p. 112), so that $K = \dfrac{k_1}{k_2}$.
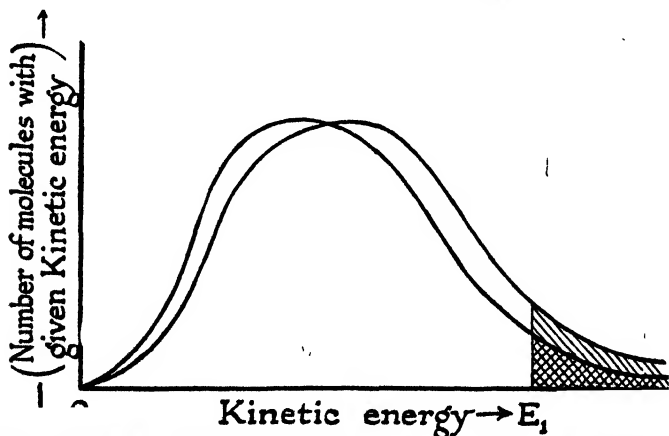
FIG. 72. DISTRIBUTION OF KINETIC ENERGY AMONG GAS MOLECULES

Taking logs in all these equations:

$$\log_e k_1 = \log_e \text{constant} - \frac{E_1}{RT} \qquad \log_e k_2 = \log_e \text{constant} - \frac{E_2}{RT}$$

$$\log_e K = \log_e k_1 - \log_e k_2 = \log_e \text{constant} - \frac{E_1 - E_2}{RT} = \log_e \text{constant} - \frac{qv}{RT}$$

$$\therefore \frac{d \log K}{dT} = \frac{qv}{RT^2};$$ a result already reached by thermodynamic reasoning. It is true that the constants used in this deduction represent the number of collisions in unit time and are therefore not independent of temperature, as we have assumed them to be, but this introduces only a small correction into the result.

The meaning of these equations will be clear from the diagram (Fig. 72), in which the kinetic energy is plotted against the number

of molecules having that energy at a given instant: a somewhat similar diagram appears in Chapter II (p. 94). The two curves represent two slightly different temperatures. It is found, as we should expect, that by far the larger number of molecules have energies in the neighbourhood of the mean energy: either very small or very large values are much less common. The total number of molecules is equal to the area enclosed by either of the curves and the energy axis, the number with a kinetic energy greater than some fixed value E_1 is equal to the shaded area. It is clear that a small fractional increase in the temperature may lead to a large fractional increase in the number of molecules with kinetic energy in excess of E_1, and this is the reason for the high temperature-coefficient of reaction velocity.

Energy of Activation.—The energy E_1 is called the *energy of activation* of the (forward) reaction. It can be calculated in two ways:

(i) From the observed temperature-coefficient of the reaction velocity and the equation $\dfrac{d \log k_1}{dT} = \dfrac{E_1}{RT^2}$.

(ii) By calculating, with the help of the kinetic theory, the total number of collisions, and finding from the observed reaction velocity at some fixed temperature what fraction of these results in reaction. This fraction can then be put equal to $e^{-E_1/RT}$, and E_1 found from this equation. Energies of activation calculated by these two methods are usually in good agreement.

Explosive Reactions.—Reaction velocity may attain very large values, and the reaction become explosive when the energy liberated as two molecules react is either greater than, or very nearly equal to, the energy of activation. The energy evolved in a fruitful collision is then sufficient to cause the reaction of neighbouring molecules, and a reaction chain is set up. If at any temperature both the heat of activation and the heat of reaction are large compared with the average energy of the molecules at that temperature, an explosive gas mixture is stable until reaction is begun by a spark or a catalyst. Explosion then takes place. A mixture of oxygen and hydrogen at room temperature is an example of such behaviour.

Applications of the Isochore.—The isochore as we deduced it is practically inconvenient and must be integrated. As a first approximation we shall assume q_v to be constant over the range of temperature considered. In many important gas reactions this

is approximately true over a wide range. Then, since $\dfrac{d \log K}{dT} = \dfrac{q_V}{RT^2}$,

$\log K = \dfrac{-q_V}{RT} + \text{constant}$. At the moment we have no means of evaluating the constant, but we can easily test the alleged linear relation between $\log K$ and $\dfrac{1}{T}$. We may take as an example the oxidation of sulphur dioxide with oxygen, a reaction of great technical importance:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$
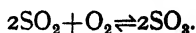
The values of the equilibrium-constant $K = \dfrac{[SO_3]^2}{[SO_2]^2 [O_2]}$ in the following table are calculated from the experimental work of BODENSTEIN and POHL:

Temperature (Centigrade)	K.
528	980
579	190
627	30·7
680	10·5
727	3·46
789	0·92
832	0·46
897	0·13

The temperature is then converted to degrees absolute, and $\dfrac{1}{T}$ is plotted against $\log_{10} K$ (Fig. 73). Though over this range the equilibrium-constant varies nearly ten-thousandfold, the isochore is satisfactorily obeyed. The importance of such a relation to the study of chemical equilibrium can scarcely be overestimated. Since the equation $\log K = \dfrac{-q_V}{RT} + \text{constant}$ (in which it is assumed that q_V does not vary with temperature) contains only two unknowns, namely q_V and the constant, only two experimental determinations of the equilibrium-constant at different temperatures are required to deduce the relation between K and T. If three determinations are made and it is found that over this range the isochore is obeyed (i.e. that the plot of $\log K$ against $\dfrac{1}{T}$ is a straight line) it is legitimate to interpolate between these temperatures, but figures obtained by extrapolation beyond the experimental results are here, as always, to be regarded with suspicion.

An interesting application of the isochore is to the dissociation of water:

$$H_2O \rightleftharpoons H^{\cdot} + OH'.$$
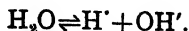
As we have already seen, the heat evolved on the combination of a gram-ion of hydrogen with a gram-ion of hydroxyl is simply the heat of neutralization of strong acids and bases, a quantity which
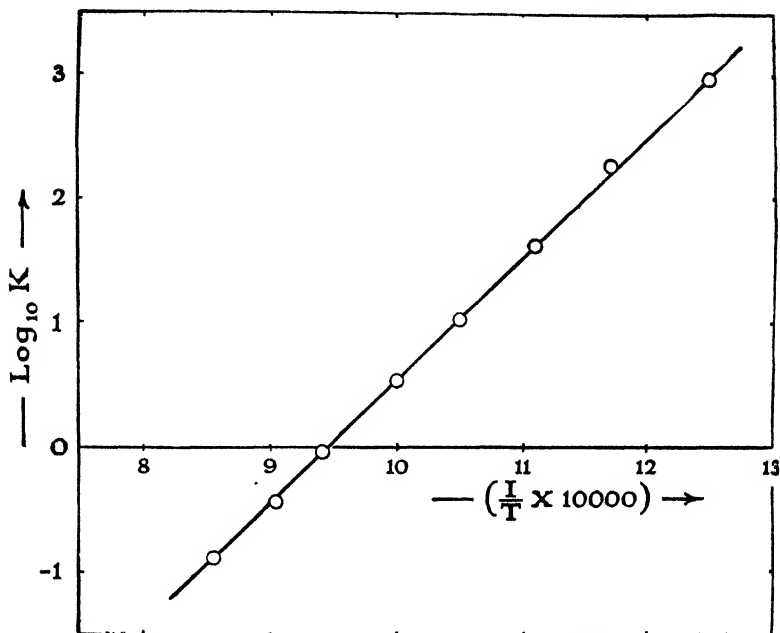
FIG. 73. THE OXIDATION OF SULPHUR DIOXIDE

can be measured without difficulty, and is equal to 13,700 calories (Chapter VI, p. 194). The relation between the temperature and the ionic product of water, K_W, should therefore be:

$$\frac{d \log K_W}{dT} = \frac{+13,700}{RT^2}.$$

When KOHLRAUSCH and HEYDWEILLER measured the electrical conductivity of pure water in 1894 Arrhenius pointed out that it should be possible to calculate the temperature-coefficient of the conductivity (from which K_W can be directly calculated) with the help of this equation, and his prediction was brilliantly fulfilled.

The following table is from his book on *Electrochemistry*, based on lectures delivered in 1897:

Temperature (Centigrade)	Sp. cond. (obs.)	Sp. cond. (calc.)
	$1 \cdot 07 \times 10^{-8}$	$1 \cdot 03 \times 10^{-8}$
$+ \ 4°$	$1 \cdot 62 \times 10^{-8}$	$1 \cdot 58 \times 10^{-8}$
$10°$	$2 \cdot 38 \times 10^{-8}$	$2 \cdot 36 \times 10^{-8}$
$18°$	$3 \cdot 86 \times 10^{-8}$	$3 \cdot 86 \times 10^{-8}$
$26°$	$6 \cdot 06 \times 10^{-8}$	$6 \cdot 01 \times 10^{-8}$
$34°$	$8 \cdot 90 \times 10^{-8}$	$9 \cdot 01 \times 10^{-8}$
$42°$	$12 \cdot 94 \times 10^{-8}$	$13 \cdot 05 \times 10^{-8}$
$50°$	$18 \cdot 07 \times 10^{-8}$	$18 \cdot 39 \times 10^{-8}$

The implication of these results is unaltered if for H˙ we substitute the actual ion $H_3O˙$.

The isochore is not restricted to purely chemical reactions, but can equally well be applied to such physical problems as the variation of vapour pressure with temperature. It is also a convenient method of calculating the heat of solution from the temperature-coefficient of the solubility. The following example, due to van't Hoff, will make this clear, viz. from the solubility of succinic acid in water at two different temperatures to calculate its heat of solution. In this calculation, which is the reverse of those we have just illustrated, we write $\log K = \dfrac{-q_V}{RT} + \text{constant}$, or, at

temperatures T_1 and T_2, $\log K_1 - \log K_2 = \dfrac{-q_V}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$. In this case K represents the solubility, which is 28·8 gm. per litre at 0° C., and 42·2 gm. per litre at 8·5° C. This makes the heat of solution 6,900 calories, while the experimental value is 6,700 calories. In the same way the heat of dissociation of a weak electrolyte can be calculated from the temperature-coefficient of its dissociation-constant as measured by the electrical conductivity of its solutions. The dissociation of a weak acid is to be represented by the equation $HA + H_2O = A' + H_3O˙$, and is usually an exothermic process. The hypothetical change (*in vacuo*) $HA = H˙ + A'$ would, of course, be endothermic. Consequently the dissociation-constants of such substances usually diminish with rising temperature. The electrical conductivity usually increases with temperature on account of the increased mobility of the ions, which is more than enough to overcome the decrease in the dissociation; but some weak electrolytes (e.g. phosphoric acid) show a maximum in conductivity with respect to temperature, a fact which was predicted by Arrhenius.

Kirchhoff's Equation and the Nernst Heat Theorem.—With the isochore we can investigate the change in the equilibrium with

temperature, but it tells us nothing of the magnitude of the equilibrium-constant at any given temperature, and we shall now briefly discuss the methods by which this problem has been attacked. We must first develop KIRCHHOFF's equation, a simple relation connecting the temperature-coefficient of the heat of reaction with the specific heats of the substances participating. Let the reaction be carried out at constant volume at temperature T, with absorption of a quantity of heat q_V. Let the products, whose thermal capacity at constant volume is Σc_2, be heated to a temperature $T+dT$, for which a quantity of heat $\Sigma c_2.dT$ is required, and at this infinitesimally higher temperature let the reaction be reversed, the heat given out being q_V+dq. Now let the original reactants, of thermal capacity Σc_1, be cooled to T, giving out a quantity of heat $\Sigma c_1.dT$; the system is now at its original condition. Hence:

$$q_V+\Sigma c_2.dT=q_V+dq+\Sigma c_1.dT, \text{ or } \frac{dq_V}{dT}=\Sigma c_2-\Sigma c_1.$$

This is Kirchhoff's equation. Now it is found that the specific heats of all substances can be expressed in a series of rising powers of the temperature, and since from Kirchhoff's equation:

$$dq_V=(\Sigma c_2-\Sigma c_1)dT,$$

it follows that q_V can also be expressed in rising powers of the temperature, thus:

$$q_V=q_0+aT+\beta T^2+\gamma T^3+ \quad . \quad . \quad .$$

For changes at constant volume carried out without the performance of external work we may substitute U for q_V so that:

$$U=U_0+aT+\beta T^2+\gamma T^3+ \quad . \quad . \quad .$$

Now from the Gibbs-Helmholtz equation (p. 231),

$$\frac{d(F/T)}{dT}=\frac{-U}{T^2}=\frac{-U_0}{T^2}-\frac{a}{T}-\beta-\gamma T- \quad . \quad . \quad .$$

Integrating, $F=U_0+aT-aT \log T-\beta T^2-\frac{\gamma}{2}T^3-$ \qquad where a is

an integration-constant.

Then: $$\frac{dU}{dT}=a+2\beta T+3\gamma T^2+ \quad . \quad . \quad .$$

and $$\frac{dF}{dT}=a-a-a \log T-2\beta T-\frac{3}{2}\gamma T^2-$$

Fig. 74 shows the type of curve which these relations give. We know from the Gibbs-Helmholtz equation that at the absolute zero F and U must be equal. NERNST was led by considerations into which we cannot enter here to suppose that the true form of

the curves was as shown in Fig. 75, which in U and F coincide not merely at, but also for some distance above, the absolute zero. If this is so, at the limit when T=0:

$$\frac{dU}{dT}=0 \text{ and } \frac{dF}{dT}=0.$$

This is the NERNST *Heat Theorem.*

Applying this relation to the differential equations already obtained, we find that $a=\alpha=0$, and

$$\frac{dU}{dT}=2\beta T+3\gamma T^2+ \quad .$$

while

$$\frac{dF}{dT}=-2\beta T-\frac{3}{2}\gamma T^2-$$

or

$$U=U_0+\beta T^2+\gamma T^3+$$

and

$$F=U_0-\beta T \quad \frac{\gamma}{2}T^3-$$

The great importance of these two equations is that they allow the calculation of F and U in terms of purely thermal quantities, viz. the coefficients β, γ . . . which can be estimated from measurements of specific heat. The primary object of physical chemistry
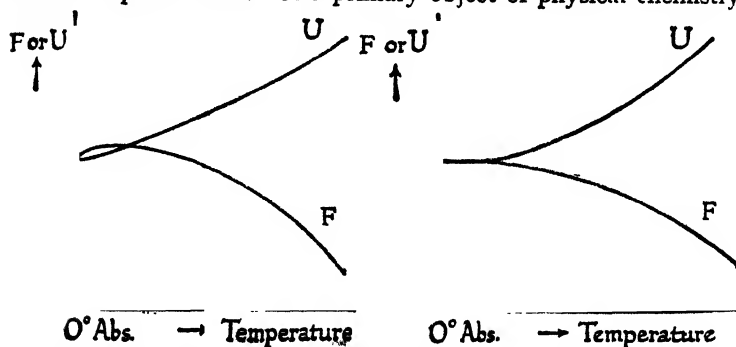
FIGS. 74 & 75. THE AFFINITY AND THE HEAT OF REACTION AT LOW TEMPERATURE

is the correlation of chemical properties with the physical forces that are the cause of chemical combination, and when this has been accomplished it will no longer be necessary, as it is necessary now, to postulate the existence of chemical forces of any kind. Since there is every prospect of our being able to trace the exact connection between the specific heat of a substance and the structure of its molecule and the internal structure of the atoms which it

contains, any exact relation between the specific heats of substances and the affinity between them is of high importance.

Applications of the Nernst Heat Theorem.—Since its introduction in 1906 the Nernst heat theorem has been constantly applied to the most diverse forms of chemical equilibrium, usually with great success. Though not directly applicable to gases (for these cannot exist at absolute zero) the law can be developed so as to include them as well. Since most of the applications require somewhat complicated reasoning, we shall examine a single instance, the calculation of the transition-temperature between rhombic and monoclinic sulphur, the experimental work being due chiefly to BRÖNSTED.

It is found that the specific heats of rhombic and monoclinic sulphur can be expressed with considerable accuracy over the required range by expressions containing only the first power of the temperature. The difference between the specific heats is $1.15 \times 10^{-5} T$. This corresponds with the term βT^2 in the series for U and F, so that $U = U_0 + 1.15 \times 10^{-5} T^2$ and $F = U_0 - 1.15 \times 10^{-5} T^2$. By determinations of the heat involved in the change of 1 gm. of sulphur (the specific heats having been calculated on this basis) we find that $U = 1.57 + 1.15 \times 10^{-5} T^2$, and consequently $F = 1.57 - 1.15 \times 10^{-5} T^2$. The most direct check on the last expression is to calculate the temperature at which the affinity F is equal to zero, since this must be the transition temperature, at which the system has no tendency to change in either direction. This

temperature should equal $\sqrt{\dfrac{1.57}{1.15 \times 10^{-5}}} = 369.5°$ Abs. $= 96.5°$ C.;

experiment gives 95.4° C., a difference of only 1.1 Centigrade degree. The important point about this calculation is that all the data employed are purely thermal.

SUGGESTED FOR FURTHER READING

LEWIS and RANDALL: *Thermodynamics.*

BUTLER: *The Fundamentals of Chemical Thermodynamics.*

PARTINGTON: *Thermodynamics for Students of Chemistry* (1950).

HINSHELWOOD: *Kinetics of Chemical Change in Gaseous Systems.*

CHAPTER VIII

ELECTROCHEMISTRY AND PHOTOCHEMISTRY

In the first part of this chapter we shall briefly consider:

    (i) The contribution of electrochemistry to general chemical theory.

    (ii) Electrochemical methods of investigating chemical systems and in analysis.

    (iii) Applied electrochemistry.

The Daniell Cell.—The DANIELL cell is familiar to all students of physics. It consists of a zinc rod dipping in a solution of zinc sulphate, which is separated by a porous partition from a copper plate surrounded by a solution of copper sulphate; the object of the partition is to reduce the mixing of the solutions. No perceptible chemical action takes place until the zinc and copper electrodes are connected outside the cell; a current then circulates, and it is found that zinc dissolves from the zinc rod while copper is deposited on the copper plate.

The passage of a current through a metal consists of a flow of electrons, or particles of negative electricity, in the contrary direction to that in which the current is said to flow—i.e. the electrons go from ' negative ' to ' positive '; and the power of supplying mobile electrons and hence conducting an electric current is one of the characteristics of a metal. Our study of FARADAY's laws of electrolysis (Chapter IV, p. 142) leaves us in no doubt as to the changes that take place at the electrodes. When a cupric ion is deposited on the copper plate as an atom of copper it takes two

electrons from the plate, and when a zinc atom leaves the zinc rod to become a zinc ion it leaves two electrons behind it:

$$Zn \rightarrow Zn\cdot\cdot + 2 \text{ electrons} \qquad \text{and} \qquad Cu\cdot\cdot + 2 \text{ electrons} \rightarrow Cu.$$
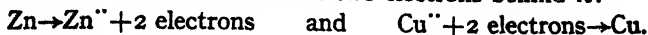
A flow of electrons from the zinc to the copper outside the cell is therefore necessary in order to prevent an excess of electrons in
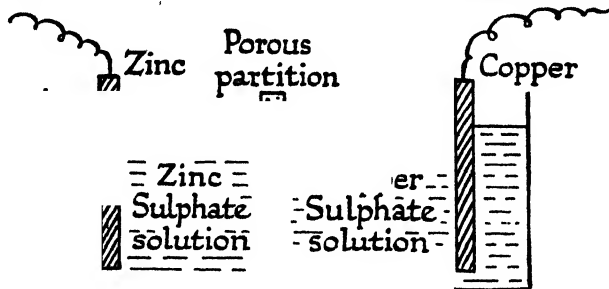
FIG. 76. THE DANIELL CELL (DIAGRAMMATIC)

the zinc rod and a deficit in the copper plate. This flow constitutes the current. The production of a current in the cell therefore depends on the fact that the tendency of a zinc atom to become a zinc ion is greater than the tendency of a copper atom to become a copper ion. A complete external circuit must be in existence before these changes can take place to any perceptible extent, otherwise the loss of a minute quantity of zinc from the zinc rod leaves an accumulated negative charge behind it which makes it impossible for any more positively-charged zinc ions to enter the solution. A similar process takes place at the other electrode.
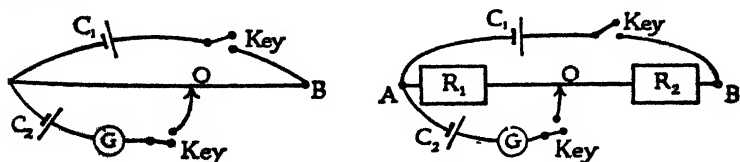
FIG. 77. THE POTENTIOMETER

The Potentiometer.—The energy relations of such a cell can be studied with advantage only if the process is made to take place reversibly and with the performance of the maximum amount of electrical work. The process is therefore opposed, until it has only an infinitesimal tendency to take place. This is the principle of the potentiometer, an instrument for measuring electromotive

I

force. In the diagrams C_2 is the cell whose electromotive force is to be determined, C_1 a source of constant electromotive force, and AB a wire resistance. The position of the sliding contact O is varied until the tendency of C_2 to produce a current flowing in one direction is exactly balanced by a current in the opposite direction imposed on it by C_1. At this point no current passes through the galvanometer G. A cell of accurately known electromotive force is then substituted for C_2 and the experiment repeated; the ratio of the E.M.F.s is then equal to the ratio of the two resistances AO. To avoid calibrating the whole length of the wire AB it is usual to concentrate nearly all the resistance between A and B in two accurately known resistances R_1 and R_2, leaving the intermediate wire for the final adjustment.

Standard Cells.—It is found that the E.M.F. developed by a cell depends not only on the nature of the solutions but also on their concentration. Consequently in standard cells—i.e. cells of constant and known E.M.F.—it is necessary to employ solutions of absolutely constant concentration, and this is most easily achieved by using slightly soluble or insoluble salts, whose solubility may if necessary be depressed by a fixed concentration of another salt with a common ion. The temperature-coefficient of the E.M.F. should also be as small as possible, for obvious reasons, and the materials must be such as are easily obtained pure. It is also essential that the passage of a current should not produce new substances —such as gas—at the electrodes, since this would alter the electromotive force.
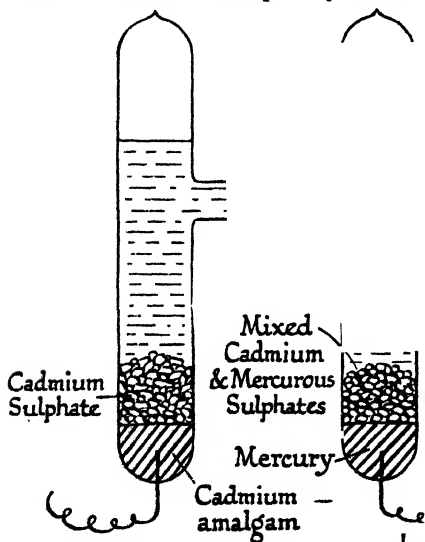
FIG. 78. THE WESTON STANDARD CELL

Cadmium Sulphate
Mixed Cadmium & Mercurous Sulphates
Mercury
Cadmium amalgam
—
+

Such a disturbance is called *polarization*, and a standard cell that became polarized would be useless. Mercury electrodes are also desirable, because mercury surfaces, being liquid, are constantly renewed, and it is found that the E.M.F. of cells is affected by any mechanical strains at the electrodes and is also slightly dependent on the nature of the metal surface.

The diagram shows the WESTON cell, in which all these conditions are observed. One electrode is pure mercury, while the other consists of mercury containing 12 per cent of cadmium (slight variations in this percentage are without effect). The intervening solution is saturated with both cadmium and mercurous sulphates, and is in contact with crystals of these substances ($CdSO_4.8/3H_2O$ and Hg_2SO_4), the former being in contact with both electrodes, the latter with the mercury electrode only. The E.M.F., which has a small but not negligible temperature-coefficient, has a value at 20° of $1\cdot0183$ volts. If not kept in a thermostat, the cell should be wrapped in cotton-wool in a box.

When the circuit is closed, cadmium atoms leave the amalgam to become cadmium ions, and mercurous ions leave the solution to become mercury atoms at the mercury electrode. These processes would alter the concentration of the solution and hence alter the E.M.F. were it not for the fact that the solution remains saturated with both sulphates owing to the presence of the solid. Nevertheless standard cells should never be allowed to supply current for more than a few moments at a time because the process of solution is a slow one.

FIG. 79. NORMAL CALOMEL ELECTRODE

Standard Electrodes.—The E.M.F. produced by a standard cell is the result of two processes, one at each electrode, and in order to investigate them separately a standard electrode or half-cell is required. The calomel electrode, the most commonly used of these, is shown in the diagram. In the 'normal' electrode a normal solution of potassium chloride is used, in the 'saturated' electrode the solution is saturated with both calomel (mercurous chloride, Hg_2Cl_2) and potassium chloride. When the electrode is in use, the tap A is closed and the tap B is open. At other times B is closed to prevent diffusion along the side-tube, which dips into the same 'bridge' solution as the side-tube of the other electrode. Two electrodes are required before any measurements can be made. If we wish to compare the E.M.F.s of two electrodes, we couple them in turn with the same standard electrode and take the difference between the E.M.F.s of the cell in the two experiments to be the difference between the E.M.F.s of the two electrodes we are investigating. An arbitrary value of zero is therefore assigned to the
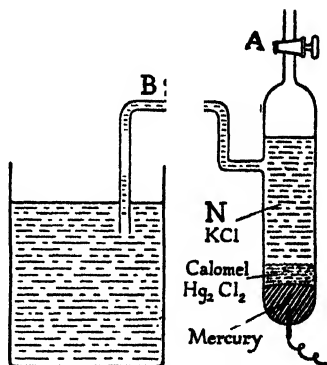
potential of one electrode and all other values are expressed on this scale. The standard hydrogen electrode is that usually selected, and
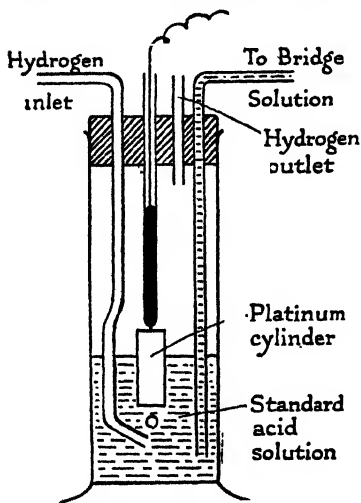
FIG. 80.   THE NORMAL HYDROGEN
ELECTRODE

this we must now shortly describe, for in addition to its use as a standard it is of great theoretical importance.

The hydrogen electrode is usually a complicated instrument; the diagram shows a simple type. Hydrogen at standard pressure bubbles up through an acid solution of standard concentration in which a cylinder of platinum foil is partially immersed. Electrical connection is made with this cylinder, and a siphon tube filled with the acid solution leads to the bridge solution in which dips the side-tube of the other electrode, whatever it may be. Hydrogen dissolves in the platinum, the solution behaving as though it were a metallic alloy, and the chemical change which takes place in this electrode is $H_2 \rightleftharpoons 2H^{\cdot} + 2$ electrons.

The Electrode Potential.—With the help of these standard electrodes it is possible to find out how the electromotive force of a metal dipping in a solution of one of its salts varies with the nature of the metal and the concentration of the solution. We shall first discuss the theory of the variation with concentration, which was first worked out by NERNST.

The relation can be most simply derived from a consideration of what is called a *concentration cell*. This includes two electrodes of

FIG. 81.   A CONCENTRATION CELL

the same metal dipping in solutions of the same salt of this metal at different dilutions V_1 and V_2 or concentrations C_1 and C_2, where

$$V_1 = \frac{1}{C_1} \text{ and } V_2 = \frac{1}{C_2}.$$ If the potential difference of a metal towards

solutions of its salts depends on their concentration, such a combination must have an electromotive force, and this is borne out by experiment. To reduce our argument to its simplest terms we shall first suppose that the sole reactions accompanying current flow are the production of cation on the side of lower concentration, and the deposition of an equal amount of cation on the side of higher concentration. In order to take into account the known divergence of ionic species from ideal behaviour as solutes we shall be obliged to replace the concentration C of cation by the quantity a, called the *activity*. The fundamental meaning of activity is that an ion at concentration C behaves identically like an ideal solute at concentration a (see also p. 157). Let the valency of the cation be n, and let the potentials of the electrodes with respect to the solutions be E_1 and E_2. Then if a gram-atom of the metal is dissolved off one electrode and deposited on the other, a charge of $n F$ coulombs has passed round the circuit ($F = 96,490$, or the number of coulombs in a faraday), and the electrical work done has been $n F (E_1 - E_2)$, since $E_1 - E_2$ is the potential difference between the electrodes, assuming (and this is only true as a first approximation) that there is no potential difference at the porous partition where the solutions meet. Simultaneously one gram-ion of the metal has been added to the solution of lower concentration, and an equal amount removed (by electrode deposition) from the solution of higher concentration. The loss F of free energy involved is that of the transference of one gram-ion from the higher concentration (activity a_1) to the lower concentration (activity a_2), namely $RT \log a_2/a_1$ (see p. 229). As these changes may be conducted isothermally and reversibly we have

$$w = -F \qquad \text{(see p. 229).}$$

or

$$n F (E_1 - E_2) = RT \log a_1/a_2$$

or

$$E_1 = E_2 + \frac{RT}{n F} \log a_1/a_2.$$

Now we shall define the standard electrode potential of a metal as its potential towards a solution with its ions at unit activity, and denote it by E_0. Therefore, when $a_2 = 1$, $E_1 = E_0 + \frac{RT}{n F} \log a_1$. This is the relation between the electrode potential of a metal and the activity of its ions. The value of E_0, however, and consequently of E_1, can be calculated only in terms of the potential of some standard electrode.

Only when the ionic concentration is small may we write $\frac{a_1}{a_2} = \frac{C_1}{C_2}$ and the formula is then in agreement with experiment. It can be

seen from the formula that the change in potential caused by, say, a tenfold reduction in the ionic activity is the same for all metals of the same valency. For univalent metals at 25° it is equal to:

$$\frac{1 \cdot 99 \times (273 + 25) \times 4 \cdot 18}{1 \times 96,490} \times \log_e 10 = 0 \cdot 058 \text{ volt.}$$

In this calculation 1·99 is the value of R in calories, $(273+25)$ is the absolute temperature, 4·18 is the number of joules in a calorie, and 96,490 is the number of coulombs in a faraday.

We have now to consider whether in practice we can limit the cell reactions in the way we have assumed. One simple device may be illustrated by an example. Suppose the electrodes are of silver, and the dissolved salt is silver nitrate. If now potassium nitrate greatly in excess of the silver salt is dissolved to give equal concentrations on the two sides of the cell, the current through the cell will be borne almost wholly by this salt; further, the movements of anion needed to balance the changes in the silver cation are accomplished with negligible change of free energy. Another advantage secured by the presence of the ' carrier ' salt is that the potential at the liquid junction is reduced to a negligible quantity (see p. 256). In a cell so prepared we may set $a_1/a_2 = C_1/C_2$, and we find the formula derived above is well confirmed by experiment.

The Activity Coefficient.—The ideal molecular free energy of a solute which is not an electrolyte is $F' = RT \log C$, where C is the molecular concentration. This expression holds fairly exactly up to about $C=1$ for most non-electrolytes. Ionic species, however, diverge from ideal behaviour even at low concentrations, and it is necessary to write $f_+c_+ = a_+$, and $f_-c_- = a_-$, f being called the *activity coefficient*, and a the *activity*. For a strong (completely dissociated) electrolyte, yielding two ions of equal charges, the total molecular free energy F' is $F_+' + F_-' = RT \log a_+ a_-$. In practice it is usually not possible to distinguish the separate activities of the cation and anion. The mean activity of the ions a is defined by the equation

$$a^2 = a_+ a_-.$$

Hence $F' = 2RT \log a$. If each ion behaved independently and ideally the free energy of the electrolyte (concentration C) would be $F' = 2RT \log C$. The ratio $a/C = f$ is termed the *activity coefficient of the electrolyte*, or, more significantly, its *thermodynamic degree of dissociation*. The standard state for ionic species is thus $a=1$, and not $C=1$ as for non-electrolytes.

As the physical and chemical behaviour of electrolytes, as of non-electrolytes, is ultimately determined by the free energy, the measurement of the activity coefficient is of fundamental importance. The most direct method, of which we give only an outline, is from the E.M.F. of suitable cells. Consider a cell formed from a hydrogen

electrode (with gas at 1 atm. pressure) and an electrode of silver coated with silver chloride, both electrodes dipping into the same solution of hydrochloric acid, of concentration C. In this cell the silver is the positive pole. If the E.M.F. is E, and one faraday of electricity has flowed, the electrical work gained is EF, and the following chemical change has occurred in the cell:

$$\tfrac{1}{2}H_2(1 \text{ atm.}) + AgCl(s) = HCl(\text{dissolved}) + Ag(\text{deposited}).$$
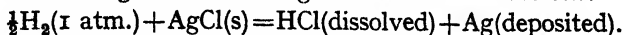
The loss of hydrogen gas, of silver chloride, and the deposition of silver will occasion the same change of free energy, whatever the concentration of the acid in the cell. If the mean activity of the ions of hydrochloric acid at concentration C is a, its production causes a gain $2RT \log a$ of free energy. Hence the total diminution of free energy F is given by

$$F = \text{constant} - 2RT \log a.$$

Hence $EF = \text{constant} - 2RT \log a$. Putting in the value of RT/F for 25° C. we find

$$\text{Constant} - E = 0 \cdot 116 \log a.$$

If $0 \cdot 116 \log C$ is subtracted from each side we have

$$\text{Constant} - (E + 0 \cdot 116 \log C) = 0 \cdot 116 \log f.$$

Now as C decreases to zero, f approaches unity, and $\log f$ approaches zero. Hence if the observed values of the quantity $(E + 0 \cdot 116 \log C)$ are plotted against C, or more conveniently, against $\sqrt{C}$, extrapolation to $C = 0$ gives the value of the constant, and then $\log f$ and hence f can be determined for any value of the acid concentration C.

Concentration	f	a	Concentration	f	a
0·001	0·965	0·000965	1·0	0·810	0·810
0·01	0·904	0·00904	1·5	0·954	1·431
0·10	0·796	0·0796	2·0	1·019	2·039
0·50	0·757	0·378	3·0	1·320	3·960

ACTIVITY AND ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID

Activity coefficients for a range of concentrations of a large number of electrolytes have been determined and tabulated. They all show similar behaviour in falling to a minimum and then rising to values above unity, as in the example of hydrochloric acid above. The above data show that the mean activity of the ions is unity when the concentration of the acid is 1·13N. The standard hydrogen electrode should therefore contain acid of this concentration.

Standard Electrode Potentials.—By coupling an electrode in which a_1 is known with a standard electrode, such as the standard hydrogen, whose potential we arbitrarily set at zero, and measuring the E.M.F. of the combination, we can calculate E_0 for the metal in question

from the known value of a_1 and the observed value of E_1. Since the term $\dfrac{RT}{nF} \log a_1$ vanishes when a_1 is equal to unity, E_0 is the potential of the metal with respect to a solution of its ions of unit activity. The following table shows some of the values on the hydrogen scale. On the convention we have adopted, a negative potential indicates a greater tendency than hydrogen has to pass into solution in the ionic form; but the contrary convention is sometimes preferred.

Metal	Ion	Potential (volts), 25° C.	Metal		Potential (volts), 25° C.
Li	Li·	−3·02	Cd	Cd··	−0·40
Rb	Rb·	−2·92	Co	Co··	−0·28
K	K·	−2·92	Ni	Ni··	−0·23
Ca	Ca··	−2·87	Sn	Sn··	−0·14
Na	Na·	−2·71	Pb	Pb··	−0·12
Mg	Mg··	−2·34	**H**	**H·**	0·00
Al	Al···	−1·66	Cu	Cu··	+0·34
Mn	Mn··	−1·08	Hg	Hg₂··	+0·80
Zn	Zn··	−0·76	Ag	Ag·	+0·80
Fe	Fe··	−0·44	Au	Au···	+1·36

This is the well-known electrochemical series of the metals; we shall consider some of the chemical consequences of these values later in the chapter. Electrodes can also be made from elements such as oxygen or the halogens, which yield negative ions, but experimental difficulties have first to be overcome, and an oxygen electrode constructed in the same way as a hydrogen electrode does not give satisfactory readings, probably because an oxide of platinum is produced. There is no evidence for the existence in water of oxygen ions, O″; if any are formed they immediately combine with water: O″+H₂O→2OH′. The results of such measurements are as follows on the standard hydrogen scale:

Element	Ion	Potential (volts), 25° C.
F₂ (1 atm.)	F′	+2·85
Cl₂ (1 atm.)	Cl′	+1·358
Br₂ (l)	Br′	+1·065
I₂ (s)	I′	+0·535
O₂ (1 atm.)	OH′	+0·400

The Effect of Ionic Transport on E.M.F.—We may now consider the effect of ionic transport upon the E.M.F. of a concentration cell, i.e. the effect of omitting the 'carrier' salt mentioned in a preceding paragraph. In Chapter IV we found that when one gram-atom of a metal dissolved off the anode and one gram-atom was deposited on the cathode, there took place at the same time a movement of the ions through the solution. Did no such movement take place, the result of the passage of the current would be to add one gram-ion to the anode compartment and remove one gram-ion from the cathode compartment; but on account of the movement of the ions the anode compartment gains only T_a gram-ions of the cation, where T_a is the transport number of the anion, and the cathode compartment loses only T_a gram-ions of the cation. The same considerations apply to the anion, so that the total transference of electrolyte from one solution to the other, when one gram-atom of the metal is dissolved from the anode and deposited on the cathode, is not one gram-molecule but $2T_a$ gram-molecules. The value of E_1 (p. 251) is therefore not $E_2 + \dfrac{RT}{nF}.\log\dfrac{a_1}{a_2}$ but $E_2 + 2T_a.\dfrac{RT}{nF}.\log\dfrac{a_1}{a_2}$.

Determination of Transport Numbers.—Consider two cells used in series, thus:

Calomel electrode–hydrogen electrode working in HCl conc. C_1
connected to
Hydrogen electrode–calomel electrode working in HCl conc. C_2

| Calomel | Bridge | Hydrogen | Hydrogen | Bridge | Calomel |
| Electrode | Solution | Electrode | Electrode | Solution | Electrode |

FIG. 82. DOUBLE CELL FOR DETERMINATION OF TRANSPORT NUMBERS

The two hydrogen electrodes are electrically connected, and when a faraday of electricity passes round the circuit, one gram-molecule of hydrogen chloride is moved from one solution to the other. The E.M.F. of the combination can without difficulty be seen to be $\dfrac{2RT}{F}.\log\dfrac{a_1}{a_2}$. Now the E.M.F. of an ordinary hydrochloric acid

concentration cell, consisting of two hydrogen electrodes in hydrochloric acid of concentration C_1 and C_2, has been shown above to be $\frac{2T_a.RT}{F}.\log\frac{a_1}{a_2}$, where T_a is the transport number of the chloride ion.

The value of T_a is therefore equal to $\frac{\text{E.M.F. of simple cell}}{\text{E.M.F. of double cell}}$. The value of the transport number of the hydrogen ion in this solution can be obtained by subtracting T_a from 1, or by experiments with concentration cells of similar type but slightly different constitution. This is the most accurate method available for the determination of transport numbers, and the results are in excellent agreement with those of the Hittorf and moving-boundary methods, but suitable cells cannot always be found for the experiments.

The Liquid Junction Potential.—A simple kinetic explanation can be given of the origin of the potential difference between two solutions of the same electrolyte at different concentrations. The electrolyte tends to travel from the more concentrated to the more dilute solution, but if the mobilities of the ions are different the more rapid ion (whether cation or anion) will tend to leave the slower ion behind. Since they are oppositely charged, this causes a potential difference which quickly reaches an equilibrium value. This potential difference will not exist for electrolytes whose ions have almost equal transport numbers, e.g. potassium chloride.

E.M.F. and Chemical Affinity.—Having made some examination of these systems from the electrical point of view, we may develop the relation between the E.M.F. of a cell and the chemical affinity of the reaction taking place in it. We have already pointed out that when the E.M.F. of a reversible cell is measured with a potentiometer the process is carried out with the production of the maximum work. Electrical work is measured in joules or volt-coulombs, and is easily calculated in these units by multiplying the number of coulombs that have traversed the circuit by the E.M.F. in volts. In electrochemical calculations the faraday is more often used than the coulomb; it is the charge required to deposit a gram-ion of a univalent metal from its solutions and (as mentioned above) is equal to 96,490 coulombs. The electrical work required is then 96,490 E, or FE, as it is generally written. If the metal is n-valent the work required per gram-atom is nFE. The numerical result will be in joules. To convert it to calories we must divide by 4·18, since 1 calorie=4·18 joules.

It was at one time supposed that the electrical energy which could be obtained from a cell, if converted to calories, would exactly equal the heat liberated in the cell reaction when this was allowed to take place freely in a calorimeter. That this idea is erroneous

can be shown from the fact that endothermic reactions can be made to liberate electrical energy. This view should be compared with the very similar and equally false opinion that the affinity of a reaction could be exactly measured by the heat which it evolved. The electrical theory appeared, however, to be strongly supported by measurements on the Daniell cell. The E.M.F. of this cell is 1·10 volts, so the electrical work obtained from the reaction

$$Zn + CuSO_4 = Cu + ZnSO_4,$$
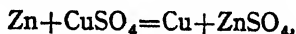
or, as we should now write it:

$$Zn + Cu\cdot\cdot \rightarrow Cu + Zn\cdot\cdot,$$
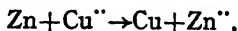
is $\dfrac{1\cdot10 \times 96{,}490 \times 2}{4\cdot18} = 50{,}800$ calories. Now the evolution of heat when this reaction is carried out in a calorimeter is 50,100 calories, so the two values are in fair agreement.

Once it is understood that the free energy change is a measure of the affinity of the reaction it becomes obvious that this agreement is fortuitous. From the GIBBS-HELMHOLTZ equation (Chapter VII, p. 235) it is known that $G - H = T\left(\dfrac{\delta G}{\delta T}\right)_p$, where G is the affinity and H the heat absorbed when the reaction takes place freely at constant pressure. Now $G = -nFE$ and $-H = q_p$, where q_p is the heat liberated in a calorimeter. So that:

$$q_p - nFE = T\frac{d(nFE)}{dT}, \text{ or } q_p = nF\left(E - T\frac{dE}{dT}\right)$$

If this equation is to be correct for the Daniell cell, in which q_p is very nearly equal to nFE, the term $nFT\dfrac{dE}{dT}$ must be very small, and the E.M.F. must have an exceedingly small temperature-coefficient. Experiments on the Daniell cell show this prediction to be correct. Since the temperature-coefficient of E.M.F. of most cells is fairly small, G is often nearly equal to the heat developed in the chemical reaction. A reversible cell is therefore a highly efficient machine for turning chemical energy into work. If the energy derived from the reaction $C + O_2 \rightarrow CO_2$ by burning coal in boilers could be converted into electricity in a suitable cell, the efficiency of the process could be trebled; but unfortunately no such cell is known and all efforts to construct one have failed.

Calculations of Equilibrium-constants.—From E.M.F. measurements we can calculate the affinity of a reaction, hence the concentrations at which the affinity is equal to zero—that is, the equilibrium concentrations—and consequently the equilibrium-constant. Our first illustration of the process will be the calculation

of the ionic product of water from measurements of E.M.F. If hydrogen electrodes in molar hydrochloric acid and molar caustic soda are connected to form a cell, and a correction is applied for the potential difference at the liquid junction, the E.M.F. is found to be 0·81 volt at 18° C. The electrical work of the cell is therefore $\dfrac{0·81 \times 96,490}{4·18}$ calories=18,690 calories. Now the cell reaction is simply the combination of hydrogen and hydroxyl ions to form water: $H^{\cdot}+OH'\rightleftharpoons H_2O$, and from our experimental data we shall be able to calculate the equilibrium-constant of this reaction, which is usually written in the form $[H^{\cdot}]\ [OH']=K_W$. The connection between the affinity of this reaction and its equilibrium-constant is given by

$$G = -RT \log \frac{K_W}{[H_2O]}$$

The extent of the dissociation of water is so small that, when it has occurred, the water has not changed appreciably from its standard state. Hence:

$$G = -RT \log_e K_W.$$

$$\log_{10} K_W = \frac{-18,690}{1·98 \times 291 \times \log_e 10} = -14·1 \text{ or } [H^{\cdot}]\ [OH']=10^{-14·1},$$

a result in excellent agreement with other methods.

The table of standard electrode potentials on p. 254 can now be put to good use. It is immediately obvious from the table which metal will displace another from a molar solution of its ions. These processes, however, are never complete (though they are often so nearly complete as to evade chemical tests), thus the equilibrium concentrations can only be calculated from a study of the affinity. The copper-zinc equilibrium, $Cu^{\cdot\cdot}+Zn\rightleftharpoons Zn^{\cdot\cdot}+Cu$, may be examined in this way. It is the reaction which takes place in a Daniell cell, and the equilibrium-constant is $K=\dfrac{[Zn^{\cdot\cdot}]}{[Cu^{\cdot\cdot}]}$. Now the E.M.F. of a Daniell cell when the copper sulphate and zinc sulphate are in approximately equimolecular concentrations is 1·10 volts (i.e. 0·34+0·76, see table), so the electrical work is $\dfrac{1·10 \times 96,490 \times 2}{4·18}$ calories=50,800 calories. Adopting our previous notation:

$$-50,800 = -RT \log \frac{[Zn^{\cdot\cdot}]}{[Cu^{\cdot\cdot}]}$$

$\dfrac{[Zn^{\cdot\cdot}]}{[Cu^{\cdot\cdot}]}=K=10^{38}$. It will readily be understood that for all practical purposes—such as those of analysis—copper is 'com-

pletely' precipitated from its solutions by zinc. It is equally obvious from consideration of the smaller table of electrode potentials for anions that chlorine will displace bromine and iodine from their salts.

Oxidation-reduction Potentials.—The theoretical treatment may now be extended to metals whose ions have more than one valency. Such elements are capable of acting as oxidizing or reducing agents, since the terms oxidation or reduction when applied to ions simply mean the removal or addition of electrons. Thus when a ferric ion takes up an electron it becomes a ferrous ion, and when a stannic ion takes up two electrons it becomes a stannous ion:

$$Fe^{\cdots}+electron \rightarrow Fe^{\cdots} \qquad and \qquad Sn^{\cdots\cdots}+2\ electrons \rightarrow Sn^{\cdots}.$$
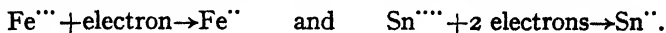
Consider an iron electrode in equilibrium with a solution containing both ferrous and ferric ions. Three changes are possible:

(i) $Fe \rightarrow Fe^{\cdots}+2$ electrons. (ii) $Fe \rightarrow Fe^{\cdots}+3$ electrons.
(iii) $Fe^{\cdots}+electron \rightarrow Fe^{\cdots}$.

At equilibrium the tendencies of these changes to take place must all be equal (or zero; the two statements are indistinguishable), and can be expressed as potentials: in terms of some standard electrode potential call them E, E', and E''. Now

$$E = E_0 + \frac{RT}{2F}.\log\ [Fe^{\cdots}]$$

and

$$E' = E_0' + \frac{RT}{3F}.\log\ [Fe^{\cdots}].$$

Multiply the first equation by 2 and the second by 3 and subtract,

then $3E'-2E = 3E_0'-2E_0 + \frac{RT}{F}.\log\frac{[Fe^{\cdots}]}{[Fe^{\cdots}]}$. Since $E=E'=E''$, we

have that $E'' = constant + \frac{RT}{F}.\log\frac{[Fe^{\cdots}]}{[Fe^{\cdots}]} = say\ E_0'' + \frac{RT}{F}.\log\frac{[Fe^{\cdots}]}{[Fe^{\cdots}]}$.

The value of E_0'' is called the standard-oxidation-reduction potential of the system $Fe^{\cdots}+electron \rightleftharpoons Fe^{\cdots}$. When the difference between the charges of the ions is n, the expression takes the form:

$$E'' = E_0'' + \frac{RT}{nF}.\log\ \frac{a_1}{a}.$$

By the use of suitable cells these equilibria can be investigated. Consider, for example, a standard hydrogen electrode in combination with an electrode consisting of a noble metal such as gold or platinum (i.e. a metal that has a negligible tendency to emit

ions into the solution) dipping in a solution containing a concentration C_1 of stannous and a concentration C_2 of stannic ions. The reaction in the tin solution is $Sn\cdots\cdots + 2$ electrons $\rightarrow Sn\cdots$, and the electrons required are liberated at the hydrogen electrode by the change $H_2 \rightarrow 2H\cdot + 2$ electrons. Since the potential of the standard hydrogen electrode is taken as zero, the E.M.F. of the cell is given
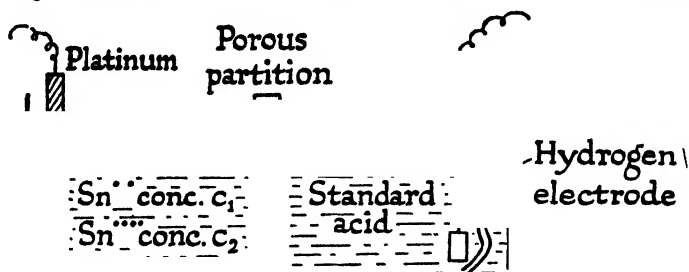
FIG. 83. CELL FOR INVESTIGATING THE STANNOUS-STANNIC ION
EQUILIBRIUM

by the equation $E'' = E_0'' + \dfrac{RT}{2F} \cdot \log \dfrac{a_2}{a_1}$. The change $Sn\cdots\cdots + 2$ electrons $\rightarrow Sn\cdots$ may be compared with the very similar change $Cu\cdots + 2$ electrons $\rightarrow Cu$, which gives rise to a potential which we have seen to be $E_0'' + \dfrac{RT}{2F} \cdot \log a_1$. The following are some standard oxidation-reduction potentials, all referred to the standard hydrogen electrode as zero. A positive sign means (for instance) that a molar solution of ferric ions is more easily reduced to ferrous ions than a molar solution of an acid is reduced to hydrogen. It should thus be impossible to liberate hydrogen from a solution of ferric ions in normal acid without first converting nearly all the iron to the ferrous condition.

Ion couple	Potential (volts)
Co···/Co··	+1·82
Ce····/Ce···	+1·55
Tl···/Tl·	+1·25
Fe···/Fe··	+0·77
TiO··/Ti···	+0·10
V···/V··	−0·25
Cr···/Cr··	−0·41

Allotropy.—An ingenious application of the theory of electrode potentials has been made to the study of allotropy. It has already been stated that tin exists in two allotropic forms, grey and white tin, whose rate of transformation is exceedingly slow at ordinary temperatures. This makes it very difficult to determine the transition temperature with any accuracy. If two electrodes, one of grey tin and one of white tin, are placed in the same solution, at a temperature at which they are not in equilibrium, a potential difference will be established between them corresponding with the affinity at that temperature of the reaction: grey tin→white tin. This can be verified experimentally, and by varying the temperature of the cell a temperature can be found at which the E.M.F. changes sign—i.e. has zero value—and this must be the transition temperature (13° C.).

Solubility of Slightly Soluble Salts.—By E.M.F. measurements it is also possible to determine the solubility of slightly soluble salts. Consider the cell:

| Silver electrode in M/100 silver nitrate | Bridge solution | Silver electrode in a saturated solution of silver chloride in M/100 potassium chloride |

This is a concentration cell for silver. If the concentration of silver ions in the left-hand solution is put at 0·01 and in the right-hand solution at [Ag·], we have $E = \dfrac{RT}{F}.\log \dfrac{0·01}{[Ag·]}$, from which [Ag·] can be calculated when E has been measured. Now the concentration of chloride ions in the right-hand solution can safely be put at 0·01, so [Ag·] [Cl′] can be calculated: this is the solubility-product of silver chloride, and is equal to the square of the solubility (Chapter VI, p. 189).

Complex Ions.—The E.M.F. method is one of the best available for the investigation of complex ions (Chapter VI, p. 197). Thus the cell:

| Silver electrode in M/10 silver nitrate | Bridge solution | Silver electrode in a solution M/10 in silver nitrate and M/5 in ammonia |

can be used to find the silver ion concentration in the right-hand solution by the method already explained. This concentration will be found very small, on account of the formation of the complex ion $Ag.2NH_3$. The formula of this complex and its dissociation-constant can be elucidated by a series of similar determinations. This is an example of how the electrode potential may be affected by the addition of a substance capable of producing a complex ion and thereby reducing the concentration of the ion with respect to which the electrode is reversible. If a concentrated solution of potassium cyanide is added to the copper sulphate solution of

a Daniell cell, the E.M.F. can be made actually to change its direction. We have shown a little way back that this will happen when $\frac{[Zn^{..}]}{[Cu^{..}]}$ is about 10^{38}. The copper cyanide complex ion leaves so minute a concentration of cupric ions in the solution that this ratio is exceeded.

Hydrogen Ion Concentration.—From the examples we have given it will be obvious that by measurements of E.M.F. we can determine ionic concentrations. The peculiar advantage of the method is its application to very low ionic concentrations—so low indeed as to be altogether inaccessible to chemical tests. In recent years the determination of hydrogen ion concentrations with the hydrogen electrode has received great attention and has become important in many branches of industry. Hydrogen at standard pressure is simply bubbled through a platinum cylinder in the liquid under investigation, which is connected by a bridge solution with a standard electrode, and the E.M.F. measured. For every unit increase in the p_H value of the solution the E.M.F. rises by $\frac{RT}{F} \log_e 10 = 0.059$ volt at $25°$ C. The hydrolysis of a salt solution can readily be calculated by such measurements. When the degree of hydrolysis is very small, as it often is, this is probably the best method available. The use of the hydrogen electrode in potentiometric titrations will be discussed shortly.

Determination of Valency.—The concentration-cell formula $E = \frac{RT}{nF} \cdot \log \frac{C_1}{C_2}$ can be used to determine the value of n, that is, the valency of an ion. This is very seldom necessary, but one or two doubtful cases do exist, such as the mercurous ion. For reasons which will be found summarized on p. 509 it is believed that this ion is not $Hg^{.}$ but $Hg_2^{..}$. The question can be settled by measuring the E.M.F. of a concentration cell of, say, mercurous nitrate with mercury electrodes. OGG, by whom these experiments were carried out, found that the E.M.F. was represented by the formula $E = \frac{RT}{2F} \cdot \log \frac{C_1}{C_2}$, not $E = \frac{RT}{F} \cdot \log \frac{C_1}{C_2}$, from which it follows that the mercurous ion is $Hg_2^{.}$. Mercury is therefore not univalent in these ions, which are best regarded as complexes produced by combination between a mercuric ion and an atom of mercury: $Hg^{..} + Hg \rightarrow Hg_2^{..}$.

Summary of Applications.—At this stage it will be as well to recapitulate the chemical applications of E.M.F. measurements which we have shortly discussed:

(i) Investigation of the equilibrium between a metal and its ions.

(ii) Determination of transport numbers.

(iii) Determination of the ionic product of water.

(iv) Investigation of the equilibrium between different ions—e.g. $Cu^{..}$ and $Zn^{..}$ or Cl' and I'.

(v) Investigation of the equilibrium between different ions of the same metal.

(vi) Investigation of the equilibrium between allotropic forms of the same metal.

(vii) Measurement of the solubility of slightly soluble salts.

(viii) Determination of the constitution and dissociation-constant of complex ions.

(ix) Measurement of hydrogen ion concentration and hence of hydrolysis.

(x) Determination of the valency of ions.

Electrical Methods in Analysis: Electrometric Titration.—Electrometric methods of titration are to-day well established. It has already been pointed out (Chapter VI, p. 206) that in the titration of a strong acid with a strong base the hydrogen ion concentration suddenly changes at the end-point. It is this which causes an indicator to change colour, but it can equally well be detected by the sudden jump in the potential of a hydrogen electrode immersed in the liquid. The diagram shows the change in the potential of a hydrogen electrode connected to a standard electrode when a strong acid is added to 25 c.c. of a strong base of equal concentration. It should be compared with the neutralization diagrams on p. 207. The E.M.F. is measured in the ordinary way with a potentiometer. The great advantage of the method is that it can be applied to strongly

24.0   25.0   26.0
— c.c. acid —➤

FIG. 84. ELECTROMETRIC
TITRATION

coloured solutions in which an ordinary indicator would be useless, and it is already much used in industry and in biochemistry. In some recent types of apparatus designed for use in works laboratories the titration has been made automatic. When the E.M.F. reaches a certain value it works a relay which stops the flow of liquid from the burette, and the operator has merely to record the burette readings; hence unskilled labour may be used. Electrometric titration has been applied to many other reactions besides neutralization, but we cannot discuss such methods here.

Conductivity Titration.—Conductivity titration methods, though different in principle, can conveniently be discussed here. It is obvious that during titration the specific conductivity of a liquid will undergo changes, and further consideration will show that a sharp break will be found in the curve connecting conductivity and composition at the end-point. If, for examp concentrated hydrochloric acid is slowly added to dilute caustic soda, hydroxyl ions are removed from the solution and chlorine ions are added to it. Since the hydroxyl ion has a much greater mobility than the chlorine ion (or indeed than any other ion except the hydrogen ion), the conductivity falls until the whole of the base has been neutralized (point A in Fig. 85). Further addition of acid then rapidly raises the conductivity. By plotting the conductivity of the solution against the volume of acid added, the position of the break in the curve, and hence the end - point, can be observed. It is not necessary actually to determine the specific conductivity at the end - point, for if a number of determinations are made on each straight line the point

FIG. 85. CONDUCTIVITY TITRATION. STRONG BASE AND STRONG ACID

FIG. 86. CONDUCTIVITY TITRATION. STRONG BASE AND WEAK ACID

of intersection can be accurately found by a graphical method. Fig. 86 shows the type of diagram obtained with a strong base and weak acid.

Similar considerations apply to precipitation reactions, such as the estimation of barium chloride with standard sodium sulphate. As the conductivity of a solution of a sodium salt is less than that of an equivalent solution of the same salt of barium, the conductivity sinks till it reaches a minimum at the end-point, when it begins to rise (Fig. 87). The flattening at the end-point is due to the slight solubility of the precipitate; a perfectly insoluble substance would give a sharp break.

The advantages of the conductivity method over titration with indicators are that it can be used with coloured solutions, for the titration of weak acids with weak bases, and for many titrations for which no indicator method has yet been devised—e.g. acetates can be titrated with strong acids to the end-point of the reaction

FIG. 87. CONDUCTIVITY TITRATION: A PRECIPITATION REACTION

$CH_3.COO' + H^{\cdot} \rightarrow CH_3.COOH$, and ammonium salts with a strong base to the end-point of the reaction $NH_4^{\cdot} \rightarrow NH_3 + H^{\cdot}$. On the other hand the temperature of the titration mixture must be kept approximately constant, the added reagent must be very concentrated compared with the other (to avoid diluting the solution), and careful consideration must be given to the mobilities of the ions concerned in precipitation titrations before the experiment can be successfully carried out.

The conductivity method of titration was first suggested by KOHLRAUSCH, the discoverer of the law of independent mobility of ions.

Gravimetric Analysis.—Electrical methods were used in gravimetric analysis before they were introduced into volumetric analysis. A consideration of the table of electrode potentials on p. 254 shows that it should be possible to precipitate copper, mercury, ·and silver from even an acid solution before hydrogen is evolved, and this can in fact be done. By weighing the cathode before and after the passage of the current, the weight of metal originally contained in the solution is calculated. The conclusion that metals with negative potentials on the hydrogen scale cannot be deposited from solution is, however, by no means always justified. While the conditions which make for a successful analysis are sometimes very complex and· are not always

completely understood, the following general principles may be stated:

1. *The evolution of hydrogen may be prevented by reducing the hydrogen ion concentration to a sufficiently low figure*—i.e. by making the solution alkaline—so long as this can be done without decreasing the concentration of the metal ions to an equal degree either by precipitation as hydroxide or by complex ion formation.

2. At certain cathodes hydrogen can be liberated only by a voltage much in excess of the theoretical: this 'hydrogen over-voltage' may be put to account by choosing a cathode on which the metal can be deposited but at which hydrogen cannot be liberated.

3. Provided that the evolution of hydrogen has been successfully prevented, metals may be separated—i.e. one can be practically completely deposited before the other—if their electrode potentials be sufficiently far apart. Since for a bivalent metal the electrode potential changes $\frac{RT}{2F}.\log_e 10 = 0\cdot029$ volt for a tenfold fall in concentration, a difference of $0\cdot1$ volt in the standard electrode potential corresponds with an approximately thousandfold concentration difference. For successful analysis it is unsafe to rely on less than a $0\cdot2$-volt difference. In electro-analysis the solution is usually mechanically stirred to avoid local inequalities of concentration.

4. In spite of this, the deposition of any given metal can nearly always be avoided by adding to the solution a salt with which it forms a scarcely-dissociated complex ion. This reduces the ionic concentration of the metal to a point at which there is no longer any tendency for deposition to take place.

Technical Applications.—In the last forty or fifty years the technical applications of electrochemistry have made enormous progress, which is still being maintained. We shall very briefly discuss in turn: 1. Refining; 2. Preparations; 3. Plating; and 4. Accumulators.

1. *Refining.*—In refining metals by electrolysis the same principles apply as were discussed under the heading of Gravimetric Analysis, viz. the conditions must be so arranged that only the desired metal is deposited on the cathode while the impurities remain in solution. Generally speaking, electro-refining is profitable only if the pure metal commands a considerably higher price than the unrefined product; thus gold, silver, copper, zinc, and tin are all purified in this way. The copper process will serve as an example. The anode consists of impure copper, the cathode of the pure metal, while the liquid is a solution of copper sulphate in dilute sulphuric acid to which are added small quantities of other substances which are found to improve the smoothness of the

deposit on the cathode. When the current is applied, copper dissolves off the anode and is deposited on the cathode at an equal rate. Impurities less 'noble' than copper remain in the solution, which must therefore be renewed from time to time, while insoluble impurities or noble metals like silver or gold do not enter the solution at all, but fall from the anode in a slimy state. This anode slime is collected and worked up for the precious metals. The product of the refining process contains about 99·98 per cent of copper.

2. *Preparations.*—The electrolytic method is invaluable for the preparation of metals whose oxides can only be reduced, if at all, with very great difficulty by the ordinary methods of chemistry. Since the electrode potentials of these metals are usually so low that they cannot be deposited from even the most concentrated aqueous solutions of their salts, the process is carried out in the fused compound and in the absence of water. Sodium, potassium, magnesium, calcium, and aluminium are all prepared on the commercial scale by the electrolysis of their fused compounds, as described later under these metals.

Alloys are sometimes manufactured by depositing the constituents simultaneously from a mixed solution of their salts, and amalgams required in the laboratory are often prepared by electrolysing a solution of the salt of the metal with a mercury cathode.

If the aqueous solution of a salt of sodium or potassium is electrolysed, hydrogen is liberated at the cathode, leaving hydroxyl ions in the solution. The electrolysis of brine (as solutions of sodium chloride are called) therefore produces hydrogen and a solution of caustic soda at the cathode, and chlorine at the anode, and is used on a very large scale for this purpose. Since chlorine reacts with caustic soda, the anode and cathode liquids must be separated by a porous diaphragm or by some other device for preventing diffusion from one to the other. The cells designed for this purpose are described under the heading Sodium. If the electrolyte is allowed to mix, hypochlorite, chlorate, and perchlorate can all be prepared under suitable conditions.

The electrolysis of sodium hydroxide solution is used for the commercial preparation of hydrogen and oxygen. The greatest advantage of the process is the high degree of purity of the gases. In the laboratory the purest possible hydrogen is made by the electrolysis of baryta solutions—since barium carbonate is insoluble no carbon dioxide can be present in the solution.

Reduction and oxidation processes at the electrodes are also put to use both in laboratory and works practice. For successful operation it is usually necessary to choose an electrode with a sufficiently high over-voltage for hydrogen or oxygen, as the case

may be, to prevent the evolution of gas, and the process is then similar to the well-known uses of 'nascent' hydrogen. The catalytic effect of the electrodes and the current density (the current divided by the area of the electrode immersed in the electrolyte) are also important factors. As an example of a reduction process we may quote the production of good yields of either azobenzene ($C_6H_5.N_2.C_6H_5$) or hydrazobenzene ($C_6H_5.NH.NH.C_6H_5$) from nitrobenzene ($C_6H_5.NO_2$). By electrolytic oxidation it is possible to prepare substances which, so far as is known, can be made in no other way. Thus persulphuric acid, $H_2S_2O_8$, is made by the electrolysis at a low temperature of fairly concentrated sulphuric acid at a smooth platinum anode that has a high oxygen over-voltage. The liberation of oxygen is thus avoided and the sulphate ions combine to form persulphate ions: $2SO_4'' \rightarrow S_2O_8'' + 2$ electrons. Since these ions would be reduced at the cathode, the electrodes must be separated by a diaphragm.

The very active element fluorine, which instantly decomposes water, was first prepared by MOISSAN by the electrolysis of a fluoride dissolved in anhydrous hydrogen fluoride, and electrolysis is still the only practicable method of preparing the gas. In 1927 an oxide of fluorine, F_2O, was prepared for the first time by the electrolysis of potassium hydrogen fluoride in the presence of a little water, and in 1929 the electrolysis of ammonium hydrogen fluoride yielded the hitherto unknown nitrogen trifluoride, NF_3.

3. *Plating.*—This can sometimes be carried out by the immersion of the object to be plated in a suitable solution, but the process is usually assisted by making the object the cathode and passing a current. In order to get a smooth coherent deposit the surface must be very clean and the metal deposited from a solution in which the concentration of its ions is very low. This can be effected by adding a salt which forms a complex with the plating ion and lowers its concentration—e.g. copper-plating baths usually contain cyanides. X-ray examination of cathode deposits has shown them to consist of a mass of small crystals of the metal. If the deposit is made from a solution in which the metal ion has a high concentration, the crystals tend to set with one of their faces parallel to the surface of the cathode, while if the metal ion concentration is reduced by the addition of a complex-forming electrolyte, the arrangement of the crystals is haphazard. This haphazard arrangement imparts mechanical strength and hardness to the deposit and increases its resistance to abrasion.

Iron can be plated with zinc to protect it against corrosion either by dipping it in the molten metal or by electrolysis, which gives a better protection; the product is popularly called 'galvanized iron.' In the same way silver mirrors can be pro-

tected against tarnishing by atmospheric hydrogen sulphide by covering them with a thin electrolytic deposit of rhodium. Tableware, jewellery, and ornamental objects are plated with gold or silver by an electrolytic process, and metal fittings are now very commonly plated with chromium or cadmium to preserve their polish.

Some books are printed from electroplates. A wax impression or negative is made of the ordinary type and is covered with graphite to render its surface conducting. This surface is then copper-plated until a thick enough plate has been produced, which can be detached from the wax by melting off the latter. Printing is then done from the copper plate, so that the original type can be used again without loss of time.

4. *Accumulators.*—When dilute sulphuric acid is electrolysed between lead electrodes, lead dioxide is formed as a brown deposit on the anode by electrolytic oxidation:

$$Pb + 2H_2O - 4 \text{ electrons} \rightarrow PbO_2 + 4H^{\cdot}.$$

The action is reversible, and is the basis of the lead accumulator, still the most widely used method of storing electrical energy.

If sheet lead is used for the plates they soon become covered, during electrolysis, by a deposit of lead dioxide which prevents any further action. They are therefore made in the form of a grid with bevelled edges, and the spaces are filled with a preparation of red lead, Pb_3O_4. This allows the electrolyte to penetrate the electrode, and during charging the anode becomes thickly covered with the dioxide, while spongy lead is produced by reduction at the cathode.

On discharge, while the accumulator is being used to supply current, the following actions take place:

At the anode: $PbO_2 + H_2SO_4 + 2H^{\cdot} + 2 \text{ electrons} \rightarrow PbSO_4 + 2H_2O.$
At the cathode: $Pb + SO_4'' \rightarrow PbSO_4 + 2 \text{ electrons}.$
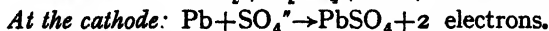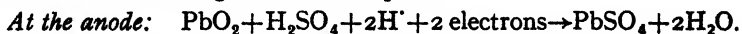
During the charging process the opposite actions take place. Since lead sulphate is almost insoluble, the concentration of lead ions in the solution is always very small. If chlorides are present in the electrolyte, chlorine is set free during charging and this attacks the lead plates: loss of water by evaporation must therefore be made good with distilled water, not tap-water.

The EDISON accumulator depends on the reaction

$$Fe + 2Ni(OH)_3 \rightarrow Fe(OH)_2 + 2Ni(OH)_2$$

that takes place on discharge, and is reversed when the accumulator is charged. The positive plate is covered with nickelic hydroxide, $Ni(OH)_3$, while the negative plate is covered with finely-divided iron, and the electrolyte is 20 per cent caustic potash with a little

lithium hydroxide. This accumulator bears mechanical shock and abrupt changes of load better than the lead accumulator, but the ratio of energy-capacity to weight is less favourable.

Reactions in the Electric Discharge.—Electric discharges of various types are also much used in the preparation of gases, both on a laboratory and on a technical scale, e.g. in ozonizers. The principal object of the use of an electric arc in the synthesis of nitric oxide was to reach a very high temperature, but specifically electrical effects come into play, and the yields obtained are in excess of those that a study of the thermal equilibrium would lead one to expect. The conception of temperature depends on the view that the molecules of a gas lose or gain energy only by collision: on this basis the probability of the energy possessed by a molecule exceeding any given value can be calculated, and the calculations are in general agreement with the temperature-coefficient of the velocity of chemical change. But in the electric discharge or the electric arc some of the molecules are ionized and consequently accelerated by the electrical force acting on them, so that no precise temperature can be assigned to gases under these conditions, nor is it reasonable to expect thermal equilibrium to be reached. Later on we shall describe more than one type of electric furnace—e.g. the phosphorus furnace or the carborundum furnace, but the function of the current in these furnaces is not electrolytic: it is used simply as a source of heat by passing a very large current through a high resistance.

PHOTOCHEMISTRY

This branch of chemistry deals with the connection between chemical processes and the emission or absorption of light. It will be convenient to draw an immediate distinction between (1) chemical processes which emit light and (2) chemical processes which are affected by the light falling on the system.

1. *Chemical Processes which emit Light.*—The heat developed in a chemical reaction (such as an explosion) is often sufficient to raise the reacting substances to incandescence, but the light given out in this way is merely a consequence of the high temperature of the system and we need not consider it here. We are more concerned with the various kinds of light emission (called *luminescence, phosphorescence,* or *fluorescence*) which take place at comparatively low temperatures. The theory of luminescence (and indeed of photochemistry in general) is still imperfectly developed, and no general explanation of these phenomena is available. A few common examples of their occurrence may suffice as an illustration.

Decomposing organic matter sometimes shines in the dark (and of course in the light as well, though the shine is then less easily seen), and the light emitted by certain insects (fire-flies, glow-worms) and marine protozoa (the so-called ' phosphorescence ' of the sea) is probably due to chemical reaction.   When concentrated ammonia is acted on by chlorine gas to form nitrogen and ammonium chloride, a bright red flash is visible, especially in a darkened room.   The feeble light emitted during the slow oxidation of phosphorus is well known, and is exhibited in a more intense form when a suspension of phosphorus in glacial acetic acid is oxidized by hydrogen peroxide.   It had been known for centuries that calcium sulphide gave out light on warming, but it has only recently been discovered that impure calcium sulphide is much more active than the pure substance.   Luminous paint, such as is used on watches, contains calcium sulphide.   When bromine reacts with acetylene a green light or ' cold flame ' is visible, and many organic compounds are known that can be made to react with luminescence.

2. *Effect of Light on Chemical Change.*—Many reactions take place only when light is allowed to fall on the reaction mixture. Hydrogen and chlorine combine slowly in diffused daylight and with explosion in bright sunlight.   A solution of mercuric chloride and ammonium oxalate is perfectly stable in the dark but deposits calomel when illuminated.

$$2HgCl_2 + \begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix} = Hg_2Cl_2 + 2CO_2 + 2NH_4Cl.$$
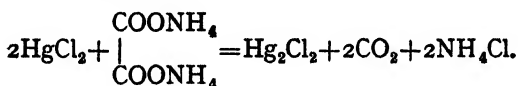
Some unstable or explosive substances can be prepared with safety only in the dark—e.g. the well-known explosive compound $N_2H_3I_3$, formerly called nitrogen iodide.   The most important of all such reactions are, however, those that go on in the living organism. Nearly all plants wither if not supplied with light, though a few are known—e.g. various fungi—which can grow in the dark, while most forms of bacteria are destroyed by light of certain kinds, such as the radiation from mercury vapour lamps, a fact which has been made use of in water-purification.   The function of the green colouring matter, *chlorophyll*, in the leaves of plants is to absorb the light necessary for the reactions by which the carbon dioxide of the air, together with water and other substances drawn from the soil, is converted to the very complex organic substances that can be detected in the plant.

The theory of the majority of these processes is unfortunately quite uncertain, though in recent years some progress has been made towards their elucidation.   Leaving on one side as beyond the range of this book the reactions that occur in living organisms,

we shall find it convenient to divide photochemical processes into those which under the influence of light reach the ordinary or so-called 'thermal' equilibrium, and those which reach an equilibrium, called the 'stationary state,' no longer stable when the light has been removed.   In the first class the light acts as a catalyst, and merely accelerates a process that could be reached more slowly—perhaps infinitely slowly—in the dark.   In the second it does work against the chemical forces, and it is as though a new variable had been introduced into the system besides the temperature and pressure familiar to us.

Decomposition of Hydrogen Bromide.—As an example of the first type we may take the partial decomposition of hydrogen bromide into hydrogen and bromine.   It was found in this as in all other photochemical reactions that the only effective light was the light that the system absorbed, and by a well-known law of physics, the absorbed wave-lengths are those which the substance itself emits when in an excited state.   It should perhaps be added that photochemistry deals not only with the wave-lengths of the visible spectrum, but also with the very active ultra-violet rays, excluding only the infra-red wave-lengths comprised under the term 'radiant heat.'   The main purpose of the investigation of the hydrogen bromide decomposition was to find out how the amount of decomposition effected depended on the amount of light absorbed.   This involves a measurement of the intensity of a certain wave-length before and after absorption, always a difficult matter.

Law of the Photochemical Equivalent.—Before discussing the results we must shortly describe the *Law of the Photochemical Equivalent* introduced by EINSTEIN in 1906.   Long before that time it was fairly clear that a certain quantity of light energy was absorbed by one of the atoms of the reacting substance, and that this atom was thereby raised to a state of activity in which it was capable of reactions impossible to it in the unexcited condition. The probable nature of this excitation will be clearer after the discussion of atomic structure in Chapter X.   Einstein connected this view with the quantum theory, then recently introduced, according to which energy could only be absorbed or emitted in definite though very small amounts, or multiples of them, connected with the frequency of the absorbed or emitted radiation by the equation $E = h\nu$, where E is the energy, ν the frequency, and h a universal constant (called PLANCK's *Constant*).   He supposed that photochemical excitation consisted in the absorption of one of these quanta by an atom, which was then capable of reaction. This theory can be tested as follows.   If the frequency of the absorbed light and the quantity absorbed are known, it is possible to calculate the number of quanta absorbed and to compare it

with the number of atoms (or molecules) which have reacted. The two numbers should be in approximate agreement.

Experimental Tests.—The first calculations were very disappointing. In the combination of hydrogen and chlorine, for example, the yield per quantum was about a million molecules of hydrogen chloride instead of one. But the new theory gave a great stimulus to photochemical research, and in a few years more than one reaction had been investigated which gave results in promising agreement with theory. In the hydrogen bromide reaction it appeared that almost exactly half a quantum was required per molecule; but since half a quantum can, by definition, exist no more than half an atom can, it is better to say that one quantum will decompose two molecules. This may appear puzzling, but it is possible to assume that the quantum absorbed by a hydrogen bromide molecule endows it with sufficient energy to convert it to atoms, and that the hydrogen atom thereby produced disrupts a second molecule without requiring any more light energy. The three steps postulated are shown below, and can all be shown to have a positive affinity—an important point in the verification of such a hypothesis.

(i) HBr+quantum→H+Br. (ii) H+HBr→H$_2$+Br.
(iii) Br+Br→Br$_2$.
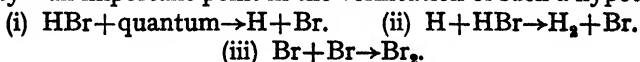
Combination of Hydrogen and Chlorine.—A similar explanation (originally suggested by Nernst) is now generally believed to account for the abnormal yield of the hydrogen chloride synthesis. In this reaction the chain mechanism begun by the absorption of a quantum continues much longer: Cl$_2$+quantum→Cl+Cl; Cl+H$_2$→HCl+H; H+Cl$_2$→HCl+Cl, etc. The same idea accounts in a convincing way for the anticatalytic effect of oxygen and other impurities, which had much puzzled earlier investigators; for the oxygen molecules may be supposed to bring the chains to an end by reacting with the free atoms of hydrogen or chlorine which alone cause it to continue. The principal difference between the photochemical syntheses of hydrogen bromide and hydrogen chloride is that the reaction Br+H$_2$→HBr+H has a negative affinity, or, in other words, cannot take place, while the reaction Cl+H$_2$→HCl+H takes place freely. Consequently the reaction chains in the hydrogen chloride system are much longer and the system is far more sensitive to light.

The hydrogen chloride photosynthesis has been the object of an immense amount of experimental and theoretical work, and it has been established that, for a given pressure of hydrogen, the reaction rate is expressible in the form

$$\frac{d[HCl]}{dt} = \frac{kI[Cl_2]^n}{[O_2]},$$

where I is the light intensity. The value of n is unity when the pressure of hydrogen is small, and $n=2$ when hydrogen is in excess. The reaction shows an induction period: that is, some time is required before it will start at all. It has been shown that this time is necessary for the chlorination of nitrogenous anticatalysts introduced into the system as impurities in the gases or from the vessel. If their quantity is reduced the reaction starts with a shorter induction period.

In the second type of photochemical reaction the system reaches different states of equilibrium in light and in the dark. Thus in ultra-violet light the hydrocarbon anthracene polymerizes to an

$$2C_{14}H_{10} \leftrightharpoons C_{28}H_{20}$$
anthracene   dianthracene
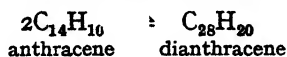
extent depending on the intensity of the illumination, while in the dark the reverse reaction takes place nearly completely. By far the most important in practice of such reactions are the decompositions of the silver halides in photography. While much remains as yet unexplained, it is possible after many years of research to give a general account of the process.

Photography.—The decomposition of the silver halides is a reversible process. When a thin layer of the halide is exposed in a high vacuum to a bright light, halogen is lost and a definite photochemical equilibrium is reached. The residue is probably a solid solution of silver in the remaining halide, but if the residue is exposed to the action of the halogen in the dark it recovers its original condition. The photographic film usually consists of particles of silver bromide, with other substances, embedded in gelatine, and when exposure to light takes place the minute quantities of bromine set free combine with the gelatine, so that the action is no longer reversible, and when the exposure is over, the film contains particles—perhaps only atoms—of silver which do not return to their previous state of combination. In all such exposures the quantities affected are too small to be directly detected by chemical methods, but if the illuminated film is treated with a suitable reducing agent, such as pyrogallol, the remaining silver halide is reduced to silver most rapidly at the points at which silver nuclei are already present, and a visible image is thereby developed, and then 'fixed.' It has recently been discovered that minute amounts of sulphur-containing compounds, normally present in gelatine, exert a special sensitizing action on silver bromide in respect to light. The theory has been proposed that small proportions of silver bromide are converted into silver sulphide, and that the light acts only on the bromide in contact with the sulphide, which is itself insensitive to light.

From the very brief account we have given of the complicated phenomena of photochemistry it should be clear that while Einstein's law offers the best hope of a more adequate understanding of the subject, yet further fundamental generalizations will probably be necessary before all the difficulties can be dealt with.

SUGGESTED FOR FURTHER READING

GLASSTONE: *The Electrochemistry of Solutions* (1945).

BRITTON: *Hydrogen Ions* (vol. i).

KOLTHOFF and LAITINER: *pH and Electro-Titrations* (1948).

BUTLER: *The Fundamentals of Chemical Thermodynamics*.

BOWEN: *The Chemical Aspects of Light* (1946).

CHAPTER IX

OUR treatment of solutions has hitherto been tacitly confined to
homogeneous systems, though it is obvious that all solutions are
ultimately heterogeneous, since they contain different kinds of
molecules. We have, however, excluded such liquids as appear
turbid or opalescent, and to these we must now turn our attention.

The Ultramicroscope.—The most obvious test of the homogeneity
of a solution is its optical clarity, but it was early recognized that
on this matter the evidence of the unaided eye was quite insufficient.
Freshly-prepared distilled water, which under ordinary conditions
appears perfectly transparent, can be shown to contain quantities
of suspended particles, and the same applies to all the liquids used
in the laboratory. ZSIGMONDY's ultramicroscope is the best in-
strument for demonstrating this. In the ultramicroscope a very
intense beam of light, concentrated by a lens system from an arc,
is passed through the liquid under examination, and a microscope
is placed with its axis at right angles to the path of the beam. If
no particles are present except the molecules of the liquid, little of
the incident light is scattered into the microscope, and an eye
applied to the instrument sees merely a dark field, but if any
discrete particles are present they appear as disks of scattered light,
and even to the naked eye the path of the beam through the liquid
is visible if the particles are sufficiently numerous. This method
originates from the TYNDALL effect, and recalls the appearance
of a beam of sunlight streaming through a chink in a shutter into
the dusty air of a darkened room. It is the best test of the so-called
homogeneity of a solution—by which we mean the absence of par-
ticles of more than molecular dimensions—but in practice it is
complicated by the difficulty of preparing even pure liquids in
so dust-free a condition that they do not show the effect. Some

liquids can be freed from dust by carrying out a precipitation in them in a closed vessel; the dust particles are usually carried down with the precipitate in a way that we shall shortly investigate more closely, leaving the body of the liquid clear, but with other liquids this is impossible.   Thus ferric chloride solutions are never optically clear, for the colloidal ferric hydroxide formed by hydrolysis is always visible under the ultramicroscope.

Classification of Colloidal Systems.—With the help of the ultramicroscope extended investigations have been made of colloidal solutions in which the solute particles vary in size between the molecules or ions of a true solution and comparatively large particles such as those present in rapidly-settling suspensions. There is, however, a large variety of heterogeneous systems which must be investigated by other methods.   Beyond giving an example or two of each we shall not be able to discuss them here.   The particles are called the *disperse phase*, the medium is called the *dispersion medium*.

Dispersion Medium	Disperse Phase	Example
Solid	Solid	Many coloured glasses (e.g. 'ruby' glass, coloured by dispersed copper)
	Liquid	Crystals with liquid inclusions
	Gas	'Solid foams'
Liquid	Solid	Sols (hydrosols): will be further discussed
	Liquid	Emulsions (e.g. oils dispersed in water)
	Gas	Foams
Gas	Solid	Smoke
	Liquid	Mist

Size of Colloid Particles.—Before alluding to PERRIN's work on the kinetic properties of colloidal solutions we shall do well to fix our ideas by making some estimate of the size of the particles in such solutions with relation to (*a*) molecular dimensions, and (*b*) particles visible in an ordinary microscope.   The diameter of the hydrogen molecule is of the order of 10^{-8} cm., while large molecules of well-defined compounds may have diameters up to, say, 10^{-7} cm.   At 5×10^{-7} cm. it is possible to detect colloidal particles with the ultramicroscope.   The smallest body visible in an ordinary microscope has a diameter of about 10^{-5} cm., and there is no hope of reducing this limit much farther, because the wavelength of light is about 5×10^{-5} cm. and bodies much smaller than this cannot be visible in the ordinary sense.   It is, however, still possible to detect their presence in the ultramicroscope as disks of light, though no direct estimate of their size, shape, or colour can be obtained in this way.   As regards their properties in solution there is in fact an insensible gradation between particles

visible to the naked eye and molecules, and it is of great importance to realize this fact. The dimensions of what are generally described as colloid particles lie between about 10^{-5} cm. and something below 10^{-7} cm.

The Brownian Movement.—A particle as large as 10^{-4} cm., if suspended in a liquid and observed in a microscope, is seen to be in continual motion. This was first noticed by the botanist BROWN in 1827, and is called the *Brownian movement* after him; the quantitative explanation of the phenomenon has been one of the triumphs of the kinetic theory. It was at first supposed that the motion was due to convection currents in the liquid, but careful experiments showed that this opinion was untenable. The motion is, in fact, thermal agitation of exactly the same nature as the thermal agitation of the molecules of a gas discussed in Chapter II. The first successful investigation of the Brownian movement was due to Perrin, and the student cannot do better than read his book *Les Atomes*, which has been translated into English.

Perrin's Experiments.—For quantitative measurements it is obviously desirable to have a suspension in which all the particles are of equal or nearly equal size and weight. Perrin used emulsions of gamboge and mastic in water, and sorted them out by a laborious process of fractional centrifuging. Since the particles are denser than water, if the emulsion is centrifuged in a long tube they tend to congregate at the outside or rapidly moving end and to leave the stationary end. Nevertheless the Brownian movement of the particles counteracts this to a degree depending on the diameter of the particle, for small ones move much faster under the influence of the Brownian movement than large ones, so that a gradient is set up along the tube in two ways: (i) particles of all diameters are more numerous at the outside end; (ii) the average diameter of the particle increases from the stationary to the outside end. By discarding all particles except those in a certain part of the tube, and by continually repeating the separation, Perrin was able to obtain a small quantity of an emulsion containing grains of very nearly equal diameter, about 4×10^{-5} cm., or rather larger than most colloidal particles. The density of the grains was measured without difficulty by the usual methods, since for this purpose a large number of grains can be used; but for the measurement of the diameter special methods had to be devised, as the grains were near the limit of microscopic visibility. Perrin found that they could be made to settle on glass in straight rows, whose length could be determined with fair accuracy. By counting the number of particles in a row the diameter of each was calculated, and this was checked by methods which we need not describe. Having prepared in this way an emulsion in which all the grains were of

equal and known size and weight, Perrin studied the vertical distribution of the grains by focusing a microscope on different horizontal layers of the liquid and counting the number of particles visible in the field. In this way he was able to find out with considerable accuracy the extent to which the lower layers of liquid were richer in grains than the upper layers.

The causes of this concentration gradient are precisely similar to those prevailing in the tube of the centrifuge, since the centrifugal force is replaced by gravity, but in this case the particles are all equal in diameter and there is no difference between the average size of the particles in the top and bottom layers. It is obvious that if the kinetic theory is correct—that is to say, if the Brownian movement of the grains is due simply to bombardment by solvent molecules—the particles, though heavier than water, will never come to rest on the bottom of the vessel, but will set up a concentration gradient such that the lower layers of liquid contain more particles than the upper ones. Now the extent of the Brownian movement depends on the size of the particles. For large particles the movement is imperceptible because the number of molecules striking them from all directions in a short interval of time is so immensely large that the probability of a resultant force in any direction is negligible. Just so a cork on the surface of a choppy sea is in incessant motion, while a large ship is scarcely affected. For small particles the effect of gravity is exceedingly small in comparison with the effect of molecular collisions, so that the difference in density between the top and bottom of a gas column a few metres high cannot be detected. Nevertheless the concentration gradient, though very slight, is easily perceptible over great heights, and the density of the atmosphere gradually decreases from the surface of the earth outwards until it reaches a figure indistinguishable from zero. The selective effect noticed in the centrifuge tube also occurs, for at great heights the air is richer in the lighter constituent nitrogen. From exact measurements of the concentration gradient of any such system it is possible on the basis of the mathematical kinetic theory to calculate the weight of the particles, assuming a known value of AVOGADRO's constant, or, knowing (as Perrin did) the weight of the particles, to calculate Avogadro's constant. The value obtained was 60.9×10^{22}, in good agreement with the value calculated by other methods. This agreement not only proves the kinetic explanation of the Brownian movement to be correct, but is also evidence in favour of Avogadro's hypothesis and the kinetic theory of liquids: that is, it supports in the strongest way the molecular theory of matter.

Dialysis.—The first systematic or extensive investigations of colloidal solutions were made by GRAHAM in the eighteen-sixties.

He was struck by the very marked differences that electrolytes and such substances as albumin or gelatine showed in the speed of diffusion through a solution, and he found that the former class would diffuse freely through membranes made from parchment paper or animal bladders, which retained the latter. The former class, whether electrolytes or not, he called *crystalloids*, the latter *colloids*, and the process of separation with a membrane he called *dialysis*. We now know that there is no rigid line to be drawn between colloids and crystalloids, either as regards their molecular weights in solution, power of passing a membrane, or optical properties. The properties of the solution change gradually from typical crystalloid properties to typically colloid properties, as the molecular weight grows larger, and such a crystalloid as cane sugar may show the Tyndall effect in very concentrated solutions.
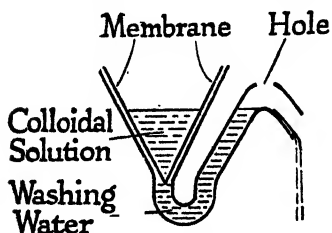
FIG. 88. DIALYSER

Animal membranes are now but rarely used in dialysis, their place having been taken by collodion or parchment paper. The process is still much used for the separation of colloids from electrolytes, an apparatus similar to that shown in the diagram being employed. A suitable funnel-shaped membrane (an ordinary filter-paper is of course useless) is placed in the funnel, and washed with a constant stream of water, whose level is automatically fixed by the perforated side-tube.

Methods of preparing Colloidal Solutions.—A large number of processes have been devised for the preparation of colloidal solutions, and it has been maintained that it is possible to prepare any substance in such a form. A great advance was made by BREDIG, who found that colloidal solutions of silver and many other metals could be prepared by passing an electric arc between electrodes of the metal under the surface of the liquid; in this process the metal is vaporized, and, on sudden condensation at a short distance from the arc, particles of colloidal size are formed. The arc method has been brought to a high degree of perfection by SVEDBERG: either alternating or direct current may be used. Colloidal solutions of mercury may be obtained by passing mercury vapour into water, or even by shaking mercury and water violently together. The chemical method is perhaps the oldest of all. FARADAY produced red and blue solutions of gold by reducing a solution of gold chloride with an ethereal solution of phosphorus, and all chemists are familiar with the colloidal solutions of sulphur produced

when solutions of hydrogen sulphide are treated with nitric acid or sulphur dioxide; they pass through paper filters and frequently cause difficulty in qualitative analysis. Electrolytic reduction has also been used for the preparation of colloids, but the commonest method of all is some form of precipitation from solution, either by cooling or by diluting the solvent with another liquid in which the solute will not dissolve. A theory of the production of colloids by precipitation has been worked out by VON WEIMARN, and as it is very wide in its applications and is in good general agreement with experiment we shall give a short account of it here, though we shall not discuss its quantitative verification, which has not always been very successful.
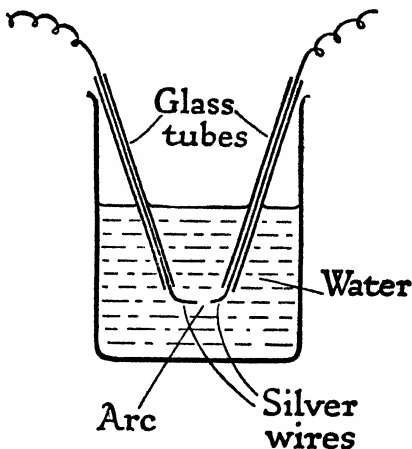
FIG. 89. BREDIG'S METHOD OF PREPARING COLLOIDAL SOLUTIONS OF SILVER (110 volts D.C.; 8 amps.)

Von Weimarn's Theory.—Von Weimarn introduces a function ∂ called the dispersion coefficient, which may be defined by the equation $\partial = \dfrac{C}{S} \cdot \eta$, in which S represents the solubility of the substance to be precipitated, and C the concentration in the instant before the precipitate forms, less the solubility, that is, the excess concentration representing the amount which will in time be precipitated from unit volume. η is the viscosity of the solution, which may be in water or any other solvent. By the use of the term dispersion-coefficient von Weimarn implies that this expression controls the fineness of the precipitate produced. A low value of ∂ implies the formation of large crystals, and vice versa. According to the theory, in any given solvent the formation of a colloidal solution should be promoted by a large excess of the substance to be precipitated and a low solubility, and this is in fact found to be true. Large crystals are made by growing them in a solution only very slightly supersaturated; small ones by rapidly reducing the solubility in a solution as concentrated as possible, either by cooling it suddenly or by adding a large excess of some precipitating agent. Von Weimarn supported his views by experiments on the precipitation of barium sulphate from solutions of manganous

sulphate and barium thiocyanate (chosen for their high solubility). In very dilute solutions fairly large crystals were obtained, since under these conditions $\frac{C}{S}$ is fairly small. As the concentration increases, the precipitated particles become smaller and smaller until in very concentrated solutions a gelatinous precipitate is obtained in which no crystalline form can be detected. The very fine precipitates are not stable, since very fine particles of a slightly soluble substance grow larger in contact with the saturated solution. This is because the solubility of a substance is greatest when it is in the form of a very fine powder: the larger the particles the smaller the solubility, though the effect is only detectable below a very small particle size. The larger particles therefore grow at the expense of the small ones, but this process is exceedingly slow unless there is a reasonable solubility, for the transfer must take place through the solution. This is why fine precipitates like barium sulphate are usually boiled for some time before filtration —the increased solubility at the higher temperature promotes the disappearance of the very small particles which will pass through a filter-paper. X-ray analysis by the powder method has shown that even small colloid particles are definitely crystalline.

Electrical Charges on Colloids.—An electric charge is usually, though not always, found to be associated with every colloid particle. This is easily demonstrated by electrolysing the colloidal solution in a U-tube and showing that the colloid has begun to migrate towards one electrode or the other, either visually if it is coloured, or by analysis if it is not. The migration is called *cataphoresis*. Generally speaking, metallic hydroxides are positively charged and consequently migrate towards the cathode, and so do some dyestuffs, while other dyestuffs, metals, sulphur, silicic acid, and most insoluble salts are negatively charged and seek the anode. By varying the conditions of formation it is sometimes possible to prepare two colloidal solutions of the same substance with charges of opposite sign on the particles. By calculation from the observed velocities one can estimate the average electric charge per particle. The results differ even between different solutions of the same substance, but colloidal charges are always much larger than ionic charges.

Coagulation.—The electrical charges on colloids, whatever their origin, are obviously closely connected with the phenomenon of mutual precipitation, for it is invariably found that colloids of opposite electrical charge coagulate each other; the particles unite and settle on the bottom of the vessel. The electrical charge appears therefore to be essential to the permanence of the colloidal state in nearly all substances, for the equivalence of mutually

precipitated colloidal solutions is electrical, that is to say, a given positive charge distributed over the particles of a colloidal solution will precipitate, and be precipitated by, an exactly equal negative charge on the particles of another solution. If an excess of one solution or the other is added, the particles, which are usually of both the kinds originally present, take on a positive charge if the colloid with positive particles is in excess, and vice versa. The electrical double layer, as it is called, which must exist on the surface of a colloidal particle appears to keep it from uniting with other particles, and as soon as the charge has disappeared the particles combine to form larger ones, a phenomenon called *coagulation*.

The power of coagulating sols is possessed in an eminent degree by electrolytes, and the effect of an added electrolyte increases with the valency of its ions, bivalent ions being much more effective than univalent ions, and tervalent ions more effective still. It is further found that the important factor is the valency of the ion of *opposite* sign to the colloid: thus the aluminium ion, with three positive electronic charges, is very effective in precipitating negative colloids, while positive colloids are more readily precipitated by the bivalent negative sulphate ion than by the univalent negative chloride ion.

The Mass of Sol Particles.—Not all particles exhibiting typical colloidal behaviour appear to owe their stability in dispersion primarily to an electric charge. Starch, agar-agar, and cellulose acetate ('cellophane') all yield stable dispersions of uncharged particles. The so-called 'soluble' starch, used in volumetric analysis, owes its solubility (or dispersibility) to the presence of phosphate groups, which do give rise to charged particles. When the particle is electrically neutral it is legitimate to expect that its true weight (or molecular weight) can be found from a careful measurement of the osmotic pressure of the sol, for Perrin's researches showed that in respect of osmotic effects colloidal particles are not abnormal, except in the magnitude of the molecular weight. In principle, a cryoscopic observation would serve the same purpose, but it must be remembered that a molar aqueous solution of any substance gives only about 1·9° of depression in the freezing-point, but has an osmotic pressure (at 0° C.) of over 22 atmospheres. Obviously the latter property is by far the easiest to observe and measure for a solute of high molecular weight. Using a membrane of cellophane, and formamide as solvent, STAUDINGER found the molecular weight of pure starch to vary within the wide limits 30,000–153,000. Actual osmotic pressures measured were of the order of 1–20 mm. of mercury.

Particles normally possessing an electric charge, that is those of

the majority of colloidal systems, would doubtless also show normal osmotic behaviour, but it must be noticed that their charges are compensated by the presence in the dispersion medium of simple, and molecularly dissolved, ions. Thus a particle of the hydrosol of ferric hydroxide very probably owes its usual positive charge to ferric ions $Fe^{\cdots}$ attached by a process of adsorption (see below). Suppose a particle holds 10 ferric ions in this way; then to each such particle there must be 30 simple anions suc. as Cl' in the dispersion medium. Each of the latter ions is otically active, and the observed osmotic pressure will be ap ximately $31 \times \varPi$ if $\varPi$ is the pressure due to one unit. Hence we c ot hope to evaluate the true molecular weight of the sol partic by this means. Fortunately other methods are available. F simple inorganic particles, such as those of metal sols, we may by the use of the ultramicroscope count the number of particles in, say, 1 ml. of the sol. Then, by coagulating a suitable quantity of the sol we can weigh directly a known number of particles, and hence obtain the average weight of each. In the case of simple inorganic sols the conception of molecular weight of the particles has no clear meaning, for we may assume, with the support of X-ray diffraction studies, that these particles are essentially very small crystalline specimens of the substance dispersed. A method highly developed (principally by SVEDBERG) for organic colloids, such as proteins, is that of the ultra-centrifuge. This machine is in principle simply a centrifuge capable of extremely high rate of rotation; it in fact creates an enormous enhancement of the natural gravitational field, and the settling of coarse suspensions under ordinary gravitation is imitated for the vastly smaller sol particles. The method has the unique advantage that it displays the molecular weight ' spectrum,' and permits the ready separation from different levels of the centrifuge vessel of the constituents of ' polydisperse ' sols. By means of this technique many biological substances of high molecular weight formerly thought to be chemical individuals have been shown to be mixtures.

The Source of the Electric Charge of Sol Particles.—Since the crystals of most substances are held stable by the presence of strong interatomic or intermolecular forces, many of which must be styled chemical rather than physical, the surface of a solid *in vacuo* must be the seat of these forces partially or wholly uncompensated. These strong attractive forces will draw substances out of gases or solutions brought into contact with the solid surface, and attach these firmly to it. This surface phenomenon is called *adsorption*. The molecules so attached may slowly migrate into the body of the solid, and become dissolved in the ordinary sense. The total process of uptake has been termed *sorption*. It has been proved in quantita-

tive experiments that an adsorptive attachment of simple ions is adequate to account for the characteristic charges on most inorganic sol particles.   It follows from this that a stable sol of this kind cannot be prepared in the complete absence of ions; on the other hand, too large a concentration of electrolyte coagulates the sol, by forcing a compensating ion on to the already charged surface. For all inorganic sols therefore there must be an optimum concentration of suitable ions, that will yield a preparation of maximum stability, i.e. one in which the charge per particle is a maximum. This view of the source of the charge is strongly supported by the common experience that too prolonged dialysis of a sol preparation renders it unstable; and by the successful reversal of the charge on sol particles by changing the ionic composition of the dispersion medium.   It has long been known that a sol of silver chloride is positively charged when precipitated from solutions containing excess of silver, and negatively charged when excess of halide is the condition of precipitation.   If the charges are assumed to depend on adsorption of (positive) silver ions, or (negative) halide ions these effects are to be expected.   It has also been shown that the cathodic direction of cataphoresis of a silver sol can be reversed by the controlled addition of small amounts of aluminium salt to the sol; here adsorption of Al$^{\cdots}$ ions is responsible for the change of sign from negative to positive.   Experiments of this kind must often be disappointing since the sol becomes highly unstable in the intermediate region of low charge, and owing to coagulation fails to pass into renewed stability with opposite charge.

There is a large and important class of colloids the particles of which secure their charge in a more direct way.   When the simple anion or cation of a salt consists principally of a long carbon chain or other complex organic unit, these ions have a strong tendency to aggregate into bundles of high molecular weight and charge. Examples are the alkali metal salts of higher fatty acids (the soaps) while the sulphonates of high-molecular-weight paraffins form the chief constituents of modern ' wetting agents,' for this power of aggregation is always associated with a large effect on the surface tension of the dissolving medium.   A number of dyestuffs have also this character.   This class of colloids is termed that of *colloidal electrolytes*.   Although the condensed ion, which may be an anion or a cation, is massive compared with simple ions, it possesses a correspondingly high electric charge, and hence its mobility is not abnormal.   Colloidal electrolytes thus behave normally in experiments on their electrical conductivity, and show evidence of full ionization.   On the other hand, the osmotic and cryoscopic behaviour will depend mainly on the simple ions, for the aggregated ion has no more effect than any of the simple ions.   The osmotic

effect of 1 gm.-mol. of sodium stearate is almost wholly that of 1 gm.-atom of sodium ion. This salt will therefore behave in a cryoscopic experiment as though it were un-ionized. These apparently incompatible predictions are completely verified in experiments. Certain organic colloids behave as *ampholytes.* Thus the proteins can form salts either with acids or alkalis. Their particles contain many definite anion-forming centres (e.g. —COOH), and cation-forming centres (e.g. —RNH$_2$). The colloidal anion of the soaps can be dissociated by extreme dilution, but protein particles can be degraded into simpler parts only by chemical action such as hydrolysis. The high electric charges upon the aggregated ions of colloidal electrolytes causes the attachment to the aggregate of large amounts of the aqueous dispersion medium: the particles are heavily 'solvated.'

Protection.—The phenomenon of *protection* must also be mentioned. It is found that certain sols, very sensitive to the coagulating powers of electrolytes, can be protected against their action by the addition of an organic colloid, chosen for its stability to electrolytes. Thus colloidal solutions of silver can no longer be precipitated by the addition of electrolytes if they contain a sufficient concentration of albumin. The explanation of this effect is not yet definitely known, but it is supposed that the more sensitive colloid is enveloped by the less sensitive and thereby protected against the action of electrolytes. The waters of the Nile are supposed to afford an example of protective action. They are always muddy because the organic matter in colloidal solution protects the suspended clay from precipitation, but when the sea is reached the salts contained in it precipitate the clay as mud and a delta is formed.

Colour of Colloidal Solutions.—The colour of sols is also worthy of attention. Many of them are bluish by transmitted and yellowish by reflected light for one of the same reasons that the sky is blue— the particles scatter the longer waves of the visible spectrum more than the shorter ones, which therefore preponderate in the transmitted light. But often the particles themselves show strong selective absorption of light, and then highly coloured sols may result, the colour depending not only on the nature of the substance, but also on the average size of the particles. Metallic sols may be prepared of almost any colour: fine red, blue, or green dispersions may be made from gold.

Applications of Colloid Chemistry.—We cannot here give any extended discussion of the many applications of colloid chemistry in industry. Dyeing is essentially a colloid phenomenon, and considerable progress has been made in explaining the theory of the process. It is at least certain that no single explanation will cover all the phenomena; it appears that the dye is sometimes chemically

combined with the fibre and sometimes adsorbed on its surface. The tanning process is another to which the principles of colloid chemistry have been successfully applied. Town water-supplies are invariably purified by filtration through beds of charcoal or sand on which the colloid particles are adsorbed. Finally, the study of life-processes is intimately connected with colloid chemistry. To take only two examples—the larger part of the oxygen dissolved in the blood is adsorbed on the surface of the corpuscles, and not dissolved in the ordinary sense; and bacteria behave as colloid particles and can be coagulated by suitable precipitants. The field is so vast that generalization is difficult, but applied colloid chemistry is one of the sciences from which the most far-reaching practical results may be expected.

Adsorption.—At this point it will be well to consider the phenomena falling under this head more fully. The fact that all solids must attract and hold to their free surfaces gases or substances from solution is the reason for many common precautions taken by the analytical chemist. Since the amount of material adsorbed is proportional to surface exposed all finely-divided substances are invariably deposited in a vacuum desiccator for some time prior to their being weighed for an analytical operation: to remove the film of water, crucibles are ignited and allowed to cool in a dry atmosphere before weighing. All precipitates will adsorb material from solution, and due precautions must be adopted to minimize this inevitable effect. It is known that many gaseous reactions are arrested by ' intensive ' drying (p. 215). It is highly probable that many of these proceed or originate on the walls of the containing vessel, and that the efficiency of that surface depends on its holding a film of water. Later we shall consider the fundamental part played by adsorption in surface catalysis (p. 289).

Adsorptive equilibrium between a surface and the bulk phase from which adsorption is taking place is reached very quickly, provided the surface is not already covered with a firmly attached film. One of the chief difficulties in conducting satisfactory experiments to elucidate the process of adsorption lies in the elaborate technique essential to ensure ' clean ' surfaces, and much time has in the past been wasted on researches in which this prime necessity has not received proper attention. By employing it as adsorbent one gram of a carefully prepared charcoal has been shown to expose a total surface of the order of 100 square metres. Nearly all this extent of surface is, of course, ' internal,' and due to the extreme porosity of the charcoal. It was natural that early experiments should be confined to the use of this adsorbent, since with it adsorptions are so large that they can easily be measured with simple apparatus. The quantity of gases taken up by charcoal

(for a given final equilibrium pressure) decreases sharply with rise of temperature, and so efficient is its adsorptive power when cooled by the aid of liquid air (—190° C.) that until recently this method provided one of the best and simplest means of obtaining a high vacuum.   By a moderate rise of temperature, and the assistance of evacuation, gases adsorbed on charcoal (or on many other surfaces) can often be recovered unchanged and without loss.   It has been observed, however, that when oxygen has condensed on charcoal, only a portion can be so easily regained.   The remainder is liberated only at high temperatures and then as carbon monoxide.   The same gas condensed on the surface of a tungsten filament (after it has been cleaned by 'flashing' at a very high temperature) can only be recovered by strong heating and in the form of volatilized tungsten oxide.   Experiments of this type indicate that at least in some cases the binding in the film is chemical in nature.   It has become customary to term this kind of adsorption *chemisorption*, and it very probably plays the principal role in surface catalysis (p. 289).

The Adsorption Isotherm.—An *adsorption isotherm* attempts to express the relation between the concentration (or pressure) of the adsorbate in the external solution or gas mixture, and the mass adsorbed per unit area of the adsorbent, at constant temperature.   No single formula has been proposed that includes all the accumulated data, although simple equations can be derived if simplifying assumptions about the constitution of the surface film are made.   For example, it may be assumed that all sites for adsorption

FIG. 90.   ADSORPTION OF A UNIMOLECULAR LAYER

are equivalent in action, and that the known short range of the forces causing adsorption limits the thickness of the film to a single molecular layer.   Langmuir was the first to show that with these premises the relation between the pressure of the external gas and the fraction a of the surface covered with adsorbed gas is as follows:

$$a = kp/(1+kp). \quad (k \text{ is a specific constant.})$$

This relation is shown graphically by the full curve in Fig. 90.   It

indicates (1) that amount adsorbed (proportional to the fraction of surface covered) is approximately proportional to the pressure at low pressures, and low adsorptions, (2) the surface reaches *saturation*, beyond which increase of pressure can have no further effect upon the amount adsorbed. There is now no doubt that in the general case the amount adsorbed follows the broken line, and the general adsorption isotherm is S-shaped. However, proportionality between a and p at sufficiently low pressures is fully proved, and as in surface catalysis we probably are concerned only with changes proceeding in the adsorbed layer in immediate contact with the adsorbent the notion that this layer will attain saturation at some stage is significant.

Adsorption Indicators.—Of recent years the theory of adsorption has been made the basis of a new type of indicator, for which we are chiefly indebted to FAJANS. We may take as an example the titration of silver salts with halides. A precipitate of silver bromide will adsorb either silver ions or bromide ions, according to which is in excess, and it will also adsorb the dye eosin, which is therefore used as an indicator in the titration of bromides with silver nitrate. The dye is adsorbed on the surface in addition to the ions, but if the silver ions are in excess the dye is adsorbed in the form of its silver salt, which is bright red, whereas eosin solutions are yellowish-rose. In the titration the eosin is added to the bromide solution, which appears yellow, and the silver solution is added from a burette. Just before the equivalence-point the colloidal silver bromide coagulates, as we should expect it to, and at the end-point the precipitate suddenly becomes bright brick-red as the first small excess of silver ions displaces the bromide ions from the surface. Chlorides can be titrated in a similar way with fluorescein, and methods have been worked out for other precipitation reactions. These methods are usually highly accurate even at great dilutions and have become very important.

Heterogeneous Catalysis.—The chemical effects occurring at the interface between solids and gases or liquids give rise to the whole series of phenomena classified under the name of heterogeneous catalysis, a fact which sharply distinguishes it from homogeneous catalysis, and justifies its treatment under a separate heading. Originally put forward by Faraday, the theory of localized interfacial action is no longer seriously in doubt, though the exact mechanism by which chemical change is brought about at the surface of the catalyst is incompletely understood.

As an example of a highly active colloid catalyst we may take Bredig's platinum solutions prepared by the arc method. The catalytic activity of a milligram of platinum in the colloidal condition is enormously greater than the activity of the same mass

of metal in a solid lump. Such a solution will rapidly decompose hydrogen peroxide into water and oxygen, and will cause hydrogen and oxygen to combine. The increased activity is due to the much larger surface of the catalyst, and it is found that the catalytic activity of platinum in the solid state is much increased by coating it with platinum black, a finely-divided form of the metal which gives the catalyst a rougher and consequently a larger surface. Bredig also found that his colloidal solutions were very sensitive to traces of certain impurities, such as hydrogen cyanide or arsenic salts, which reduced or even destroyed their catalytic power, a phenomenon which he called ' poisoning '—by analogy with the somewhat similar effect of such substances on living organisms. There can be little doubt that these catalytic poisons owe their properties to the fact that they are more readily adsorbed on platinum than are the reactants of the catalysed reaction, which are consequently unable to reach the surface when the poisons are present. From approximate calculations of the minimum effective thickness of the poison layer it appears that a layer one molecule thick is sufficient if it covers the whole surface of the catalyst; a result which in view of ADAM's experiments on fatty acid films on water (p. 106) will cause no great surprise.

The study of gas reactions in recent years has shown that a surprisingly large proportion of them are chiefly, if not wholly, heterogeneous, and take place on the walls of the vessel if no more effective catalyst is provided. The best way of testing the alleged homogeneity of a gas reaction is to fill the reaction vessel with sharp-edged fragments of the material from which the vessel is made, or to alter its size, and to see whether the reaction velocity is thereby affected when allowance has been made for any change in volume. The investigation of reactions in solution is more difficult, since the removal of dust particles from liquids requires a highly specialized technique, but interesting results have been obtained. Thus RICE has shown that the notoriously unstable substance hydrogen peroxide can be kept nearly unchanged for indefinite periods in concentrated solution if all floating impurities are absent, and that under these conditions its stability is little affected even by heating. Commercial hydrogen peroxide always contains preservatives or anticatalysts which retard its spontaneous decomposition; among the substances used for this purpose we may mention sulphuric acid, alcohol, ether, glycerol, acetanilide, and barbituric acid. The mode of action of such diverse compounds has always been a puzzle, and Rice's explanation that they merely poison the dust particles which act as heterogeneous catalysts by adsorption on their surface is almost certainly the correct one.

The Characteristics of Surface Catalysis.—In spite of intensive

laboratory studies and the enormous multiplication of examples of this type of catalysis in industry, no generally acceptable theory of the process has been established; indeed, the opinion is growing that for such a wide range of diverse phenomena no single theory can be adequate. In practice therefore the selection of a catalyst for a given chemical change is largely a matter of trial and error. We must be content to present a summary of the outstanding features of this form of catalysis, followed by comment.

(1) The chemical action is localized in the interfacial region where the reactants, and often the resultants also, are held for a period in direct contact with the catalyst surface.

(2) If the reactants are present in this region in greater density than in the bulk gas or solution, this increase of concentration is not the cause of the catalysis.

(3) The kinetic order in respect to the external pressure or concentration in bulk is often zero, or a low fraction.

(4) The alternate formation and decomposition of intermediate compounds of normal type cannot give a general explanation of catalytic reactions (cf. homogeneous catalysis, p. 214).

(5) The energy of activation for a catalysed reaction is less than for the homogeneous (uncatalysed) reaction. (For the explanation of activation see p. 239.)

(6) Reactants in contact with the catalysed surface adopt an ordered arrangement.

(7) The activity of catalysts is highly specific, and the activity of mixtures is not usually predictable from the activities of the constituents.

It is now generally conceded that heterogeneous catalysis depends upon surface phenomena, and not appreciably on bulk dissolution of reactants by the contact substance. Nevertheless those effects on the physical form of the catalyst that might be expected from a vigorous bulk interchange with a gas phase are often actually observed. Ammonia is oxidized to nitric oxide, and sulphur dioxide to sulphur trioxide, by the joint agency of atmospheric oxygen and platinum. Each of these oxidations is the basis of very large-scale industrial operations for the manufacture of nitric and sulphuric acids. In both processes the initially smooth, bright platinum surface is intensely roughened during the catalysis. In the nitric acid industry this effect has to be carefully controlled, for the rough metal tends to oxidize the ammonia to nitrogen rather than to nitric oxide. If finely-divided platinum is deliberately used as catalyst hardly any nitric oxide is produced. On the adsorption

theory alone it is not easy to explain this important change of chemical reaction. The kinetics of many surface reactions, and particularly the ' poisoning ' effects of some of the products, can be rationally and simply explained by assuming that the reaction proceeds in an adsorbed film only one molecule thick, but this satisfactory result cannot be taken as proof of the unimolecular nature of the film. That adsorption films formed by a variety of substances on many surfaces at ordinary temperatures have more than this minimum thickness has been abundantly proved by joint measurements of surface area and amount of adsorption. With our present knowledge of molecular diameters it is easy to ascertain the order of magnitude of the molecular concentration on a fully covered surface, and to show that such an increase of concentration could in no way explain the often enormous increase of reaction velocity effected by a catalyst. The law of mass-action (p. 113) proves that a zero order of reaction must be fictitious; such an experimentally determined order can only mean that in the mechanism of the reaction the concentration of the reactant associated with the zero order is held automatically constant. Such constancy would be achieved if the adsorption film were ' saturated,' and therefore its concentration independent of the external pressure. A low fractional kinetic order would indicate that the film is maintained near to the saturation point. It is difficult to see how these characteristic orders of reaction could be explained otherwise, so their common occurrence in heterogeneous catalysis strongly supports the adsorption hypothesis. The union of hydrogen and oxygen is strongly catalysed by many metals, and the action may be vigorous at temperatures far below the reduction point of any normal oxide of the metal. In such cases an alternate oxidation of metal and reduction of (normal) oxide is excluded. ' Surface ' hydrides and oxides formed by chemisorption (p. 288) are, however, commonly assumed to play the principal part in such changes. The basic feature of all examples of catalysis is the enhancement of the reaction velocity at a given temperature. Many studies of the change of the velocity of catalysed reactions with temperature prove that the main cause of the increase of velocity is a diminished energy of activation. Some otherwise puzzling features of this type of catalysis can be explained when it is assumed that in the adsorbed film the reacting molecules are attached to definite sites in an orderly manner related to their chemical structure. Thus it has been shown that in the dehydrogenation of the lower alcohols (to produce aldehydes and hydrogen) in contact with copper at 200° to 300°, the alcohols undergo the change at nearly equal rates at the same temperature. This result points to the conclusion that these alcohols are attached to the metal solely by

means of the group —CH_2OH, which is also the part of the molecule actually changing.

$$CH_3CH_2OH = CH_3CHO + H_2.$$
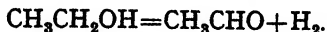
The Use of Isotopic Exchange Reactions in Catalysis.—One of the chief obstacles to progress in elucidating surface catalysis has been a lack of sufficiently simple catalysed reactions. The discovery of 'heavy' hydrogen or deuterium has made possible the study of 'exchange' reactions, such as

$$H_2 + D_2 = 2HD,$$
$$H_2O + D_2O = 2HDO,$$
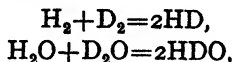
wherein the reactions are merely interplays between atoms nearly identical. When a mixture of hydrogen and deuterium is exposed to chromic cxide or finely-divided nickel at temperatures as low as $-190°$ C. the exchange proceeds at a measurable rate, and is very rapid on gently-heated nickel. The homogeneous reaction requires temperatures at least as high as 600° C. A detailed and quantitative study of the catalysed reaction, especially the determination of the activation energy, has demonstrated that the reaction on the surface cannot be that shown in the above equation, but needs the intervention of atomic hydrogen and deuterium even at the very low temperature. The conclusion is that the dissociation accompanies adsorption. The well-known pre-eminence of nickel as a hydrogenating catalyst is thus very probably due to its dissociating power for hydrogen. Much more investigation will be needed before a well-established theory of even this one type of surface catalysis can be expected.

The Kinetic Order of Surface Reactions.—It will be recalled that the law of mass action (p. 113) requires reaction rate to be expressed in the form

$$\text{Rate} = k(C)^n,$$

where C is the concentration of the reactant *at the seat of reaction*. For a reaction proceeding solely at an interface, C is obviously synonymous with concentration in the adsorbed layer. Hence we can only learn the true order of a catalysed reaction from observations on the change of external pressure if we already know the form of the adsorption isotherm, or we are confident that the observations have been made at such low pressures that adsorbed amount and pressure are proportional. As a probable example of the latter condition we may cite the decomposition of phosphine into its elements. This gaseous reaction is now known to proceed almost exclusively on the walls of the glass or silica vessels containing the reacting gas (p. 290), and a general study of the adsorbing powers of these solids proves that they are feeble, and

high pressures are required to produce a dense adsorbed layer. Hence the kinetic first order found from observations on the pressure almost certainly reflects the true order on the surface. The decomposition of nitrous oxide at moderate temperatures upon a gold surface is probably another example of the same sort. This latter case is of interest because decomposition of this oxide into its elements can also proceed homogeneously, but at higher temperatures. It is found to show the second kinetic order in these circumstances. On the surface we have reactions (1), and homogeneously reaction (2):

$$N_2O=N_2+O; O+O=O_2 \qquad (1)$$
$$2N_2O=2N_2+O_2 \qquad (2)$$
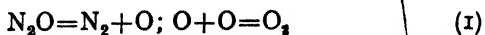
Now it can be shown that (1) proceeding homogeneously would involve an increase of free energy, and in this case is therefore ' forbidden.' The strong attachment of the oxygen atoms to the surface (whereon they subsequently unite in pairs and leave the surface) is a process associated with sufficient decrease of free energy to ensure that the reactions (1) can proceed spontaneously on the surface. It is common for a catalysed reaction to show an apparent zero order, or low fractional order of reaction. Two alternative conclusions are then possible: (a) the adsorption is feeble, and the true order is that found by pressure studies, (b) the adsorption is strong, and has reached saturation of the contact layer, wherein the concentration of the reactant is then held constant. As an example of this behaviour we may take the decomposition of ammonia into its elements on metallic surfaces, such as tungsten. That of the above alternative explanations we should choose (b) is indicated in this case by the fact that at very low pressures the apparent order rises sharply, and doubtless would ultimately reach the true order, if experiments did not become too difficult owing to the very low pressures required. Thus in general when the apparent order is fractional or zero we can hope to learn little about the reaction process on the surface unless experiments are extended to very low pressures.

Poisoning by the Products.—Most interesting results are obtained when the reactants or products compete for the surface of the catalyst. HINSHELWOOD and PRICHARD studied the velocity of the reaction $CO_2+H_2 \rightarrow CO+H_2O$ (made irreversible by removing the water as it was formed) on a platinum catalyst; the diagram (Fig. 91) shows the type of curve obtained when the initial rate of reaction is plotted against the initial pressure of carbon dioxide at a fixed temperature, the initial hydrogen pressure being kept constant. It will be observed that the initial rate shows quite a sharp maximum, the explanation being that beyond this point the carbon

dioxide takes up so much of the available surface of the catalyst that the hydrogen cannot find room on it. The reaction velocity is therefore reduced, for we must presume that two molecules will only react when they find themselves in adjacent positions on the catalyst.

Heterogeneous Catalysis in Industry.—Some of the very numerous industrial applications of heterogeneous catalysis will be discussed in the section on the inorganic compounds; such are the synthesis of ammonia, the oxidation of ammonia, and the contact process for sulphuric acid. Among the organic applications the most important is perhaps the use of finely-divided nickel as a catalyst for hydrogenation, investigated by SABATIER; this process is used on a very large scale in the soap and margarine industry for converting liquid oils into solid fats by combination with hydrogen under pressure in the presence of nickel. The principal disadvantages of catalytic methods in industry are the high cost of the catalyst, if one of the platinum group of metals must be used, and the necessity of purifying the reactants to avoid ' poisoning ' of the catalyst; but the advantages of these methods are usually found to outweigh their defects.
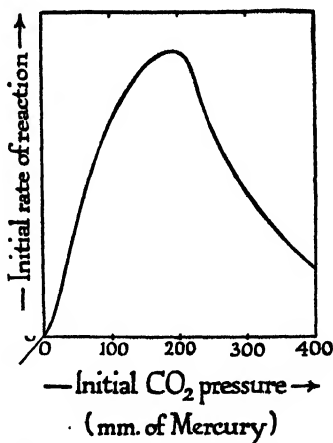
FIG. 91.   RATE OF REACTION BETWEEN HYDROGEN AND CARBON DIOXIDE ON PLATINUM

SUGGESTED FOR FURTHER READING

HINSHELWOOD: *The Kinetics of Chemical Change in Gaseous Systems.*
WARD: *Colloids, their Properties and Applications* (1948).
ALEXANDER: *Surface Chemistry.*
ALEXANDER and JOHNSON: *Colloid Science* (1949).

CHAPTER X

RADIOACTIVITY AND ATOMIC STRUCTURE

In the eighteen-seventies chemical theory was at once simpler
and more firmly held than at any time before or since.   Not only
was it almost universally supposed that the existence of atoms was
established beyond doubt, but they were held to be indestructible
and of the same weight as other atoms of the same element—a point
on which no direct evidence was available.   In the following decade
the closer investigation of the conduction of electricity through
gases under low pressure indicated new and startling problems,
whose solution required many years of experiment and speculation
and is not yet in its final form.   Progress in the early stages was due
solely to the physicists, but later on the close connection of the
subject with chemistry became evident, and modern progress has
come from both directions.   The work to be discussed in this
chapter is very extensive and we shall not be able to preserve the
chronological order.   We may begin with the discovery of the
electron.

Cathode Rays.—Every one is familiar with the brilliantly coloured
light produced by the passage of electricity through a discharge
tube containing a gas under low pressure; it is now many years
since these tubes were first used by advertisers, who seem to prefer
the red neon light above all others.   At an early stage of the in-
vestigation of this discharge two types of ray were discovered
in the tubes themselves: the cathode rays and the positive rays.
The former started at the cathode and were projected in a direction
perpendicular to the cathode surface: they travelled in straight

lines, cast definite 'shadows with no sign of diffraction, would pass through windows of thin metal foil, and if concentrated on an object by using a concave cathode would rapidly make it white-hot.   They would blacken a photographic plate, caused certain substances to fluoresce, and endowed gases through which they passed with some power of conducting electricity.

It was therefore deduced that cathode rays were material in nature, and consisted of streams of negatively-charged particles. The rays could be deflected by magnetic or electrostatic fields, and by measuring the deviations produced it was found possible to calculate their charge and their mass. Both of these were found to be
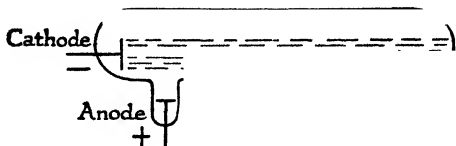
FIG. 92.   CATHODE RAYS

the same for every particle, whatever the nature of the cathode at which it originated or the rarefied gas through which it travelled. The charge is usually denoted by *e*, and is equal to the charge required to deposit one atom of a univalent metal from solution.   The mass was found to be about 1/1850 of the mass of a hydrogen atom.

These particles were called *electrons*, and in these and subsequent experiments it was shown that electrons could be obtained from the atoms of all elements.   The investigation of the positive rays proved more difficult, as homogeneous beams could not be obtained. The simplest apparatus in which the rays can be observed contains a perforated cathode through which they stream from the direction of the anode: but for quantitative experiments the perforations are reduced to a single narrow passage in a copper tube.   The apparatus devised by SIR J. J. THOMSON, to whose brilliant researches we owe the first clear understanding of the positive rays, was the original form of the apparatus later improved by ASTON, and now known as the *mass-spectrograph*; it will be described later in this chapter when we come to deal with isotopes.   By subjecting a narrow beam of positive rays to transverse electrostatic and magnetic fields, Sir. J. J. Thomson caused them to deviate from their original direction and then received them on a photographic plate.   If, like the cathode rays, the positive rays consist of charged particles, the mass and the charge (or rather the ratio of one to the other) can be calculated from the observed deviation of a particle of known velocity.   Since the velocity is, in fact, by no means uniform, particles with equal values of the mass to charge ratio will not be concentrated on a single spot on the photographic plate, but will be spread over a parabola from whose dimensions the ratio can be calculated.

Positive Rays.—In this way the positive rays were shown to consist of atoms and molecules from which one or more electrons had been removed, though on later occasions parabolas were obtained to which no satisfactory origin could be attributed. At the time of their discovery positive rays completed the chain of evidence which showed that atoms could be disintegrated into negatively-charged particles (electrons) of minute mass and positively-charged residues in which almost the whole mass of the atom remained. In more recent years their study has taken us one stage further still in our investigation of the interior of the atom. Sir J. J. Thomson's experiments provided the first proof for the assumption made since the beginning of the atomic theory that the atoms of some elements at least are individually as well as statistically equal in mass.
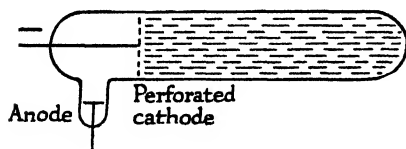
FIG. 93. POSITIVE RAYS

At an early date attention was given to the range of cathode rays, that is, to the distance through which they could travel through air or some other gas before they were absorbed, and to the thickness of metal foil which they could penetrate. This power of penetrating thin sheets of metal without perforating them, which had once been used as an argument against their material nature, was readily understood when measurements had been made of their mass, so small compared with that of the atom, and their very high velocity, often not much less than that of light. From the kinetic theory of gases and the known values of the diameters of gaseous molecules it was possible to calculate how many molecules an electron would on the average encounter in its passage through a gas, and the results showed that by far the larger part of an atom must be transparent to electrons. It was even possible to estimate the diameter of that part of the atom through which the electron could not pass; this was found to be a minute fraction of the atomic diameter. We thus arrive at a picture of a small but impenetrable nucleus surrounded by a relatively large and nearly empty area, a conclusion entirely confirmed by the investigations of LORD RUTHERFORD of the collisions between neutral atoms and positive particles.

Scattering of α-Particles.—The discovery of radioactivity in the closing years of the nineteenth century had provided a source of positive particles more convenient than the discharge tube. It had been shown that certain radioactive substances emitted streams of positive particles, called α-particles, which consisted of atoms of

helium from each of which two electrons had been removed, and which therefore carried a double positive charge. These particles, like cathode rays, can penetrate very thin metal foil, and in so doing they suffer a succession of small deviations, so that a narrow beam, after passing through foil, will be to some slight extent spread out. The scattering can be predicted from the laws of
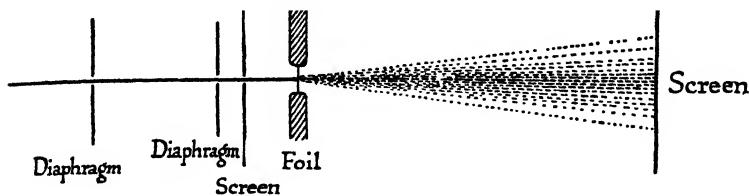
FIG. 94.   THE SCATTERING OF α-PARTICLES

probability, and the observed values can be accounted for in this way, but certain particles are deflected through more than a right angle, and will strike a screen placed on the *near* side of the foil. The probability that the sum of a succession of small deviations should reach so large a value is, under the experimental conditions, vanishingly small, and it is concluded that these large and com-paratively rare de-viations are due to encounters between α-particles and bodies of small size (since these encounters are infre-quent) but heavy charge (since the deviation produced is large). These are identical with the nucleus whose probable existence has been revealed by cathode ray experiments: by measurements of the deviations Rutherford was able to show that the positive charge on the nucleus, using the electronic charge as unit, was about half the atomic weight of the metal of which the foil was made.

FIG. 95.   DEFLECTION OF AN α-PARTICLE

α-Particle Tracks.—Both cathode rays and α-particles have the power of ionizing gases through which they pass, that is, they split up the atoms with which they collide into negative particles (elec-trons) and positive particles. This property can be used to make the track of α-particles visible by C. T. R. WILSON's method, in which, by the sudden expansion of a gas saturated with water-vapour, drops of water are made to condense on any ions which may be present. In this way the track of the particle through the

of their atomic weights those of similar properties were separated by six places:

Li Be B C N O F
Na Mg Al Si P S Cl
K Ca etc.

Unfortunately Newlands associated his theory with a somewhat fanciful allusion to the octave of the musical scale, and it was coldly received: indeed the ironical suggestion was made that he should try the effect of arranging the elements in the alphabetical order of their initial letters. Somewhat greater interest was aroused by the classification independently put forward by the Russian MENDELEEFF in 1869. Mendeleeff's table contained several blank spaces which he assigned to elements at that time undiscovered, and he boldly predicted the properties of three of these elements on the basis of the properties of their neighbours in his classification. Within a few years the three elements were discovered, and a study of their properties showed that Mendeleeff's predictions were abundantly verified. Germanium, discovered in 1886, was described by Mendeleeff in 1871, fifteen years before its discovery, as an element with an atomic weight of about 72 and a density of about 5·5. Its oxide, of formula MO_2, was to be a refractory white solid with a density of 4·7, and it was to be feebly basic; its fluoride MF_4 was to be a liquid with a boiling-point below that of water and a density of 1·9. All these predictions were true, and others were made which were either true or nearly true of the then undiscovered elements scandium and gallium.

Anomalies in the Periodic Classification.—From that time on the periodic table has been generally accepted, though, until Moseley's work and after, its significance was quite obscure. There were three anomalies in the table:

(i) If the order of the atomic weights is taken, three pairs of elements fall out of order, and have to be interchanged, but if Moseley's atomic numbers are taken, this anomaly disappears.

(ii) No satisfactory place can be found for hydrogen.

(iii) The rare earth elements do not fit into the table, and have to be accommodated in a separate division of it. All these anomalies are in satisfactory agreement with modern theories of atomic structure.

The Periodic Table.—Several methods of arranging the periodic table have been suggested: we reproduce one of the best. The figures are the atomic numbers, and the anomalous order of the atomic weights of the pairs K and A; Ni and Co; I and Te, should be verified from the table of atomic weights. The horizontal rows

Group O Group I Group II Group III Group IV Group V Group VI Group VII

He 2   Li 3   Be 4   B 5   C 6   N 7   O 8   F 9

Ne 10   Na 11   Mg 12   Al 13   Si 14   P 15   S 16   Cl 17

A 18   K 19   Ca 20   Sc 21   Ti 22   V 23   Cr 24   Mn 25 | Fe 26   Co 27   Ni 28 | Cu 29   Zn 30   Ga 31   Ge 32   As 33   Se 34   Br 35

Kr 36   Rb 37   Sr 38   Y 39   Zr 40   Nb 41   Mo 42   43 | Ru 44   Rh 45   Pd 46 | Ag 47   Cd 48   In 49   Sn 50   Sb 51   Te 52   I 53

Xe 54   Cs 55   Ba 56   [La Ce 57 58 * | Hf 72]   Ta 73   W 74   Re 75 | Os 76   Ir 77   Pt 78 | Au 79   Hg 80   Tl 81   Pb 82   Bi 83   Po 84   — 85

Em 86   87   Ra 88   Ac 89   Th 90   Pa 91   U 92

Group VIII

THE PERIODIC TABLE (AFTER WERNER, 1905)   Atomic numbers 59 to 71 inclusive.

* The Rare Earth Elements.

are called periods, the first two the short periods, the others the long periods. The whole table is also divided vertically into groups numbered from O to VII, the first member of each group being an element of the first short period, as follows:

Group	O	I	II	III	IV	V	VI	VII
Element	He	Li	Be	B	C	N	O	F

The elements connected with these either vertically or obliquely belong to the same group, so that Group I includes Li, Na, K, Rb, Cs, Cu, Ag, and Au. The first two elements in Groups I to VII are called the typical elements of their group, and after these the left-hand branch is called Subgroup A, the right-hand branch Subgroup B. The elements enclosed by a dotted line were called the transition elements, and are sometimes classified as Group VIII. The section labelled ' rare earths ' includes the thirteen elements with atomic numbers between 58 (Ce) and 72 (Hf), and is not classified with any group, though often considered with Group III. Lanthanum, cerium, hafnium, and (less correctly) thorium are sometimes classified with the rare earths. In this book cerium, hafnium, and thorium will be included in Group IV, the remainder in Group III.

The object of the periodic table is to bring out the similarity in chemical and physical properties between elements of the same group, and the gradual change in properties in passing up or down one group or in passing from one group to the next. Nearly all properties of the elements and their compounds are in some degree periodic, though there are important exceptions, such as the specific heat (p. 66) and the X-ray spectrum. It is not proposed to give an extensive discussion of these points here. The periodicity of properties is made the basis of the succeeding chapters, and the full meaning of the periodic table will be understood only when we have dealt with the phenomena of radioactivity and the theory of atomic structure. It should, however, be noted that the maximum valency of an element usually corresponds with the number of its group, so that in the long periods the valency series from I to VII is gone through twice: the valency of the metals in Group VIII is variable.

Radioactivity.—BECQUEREL, in the course of a study of fluorescence, observed in 1896 that certain compounds of uranium emitted radiations which would blacken a photographic plate wrapped in opaque paper and ionize the air in their neighbourhood. In the previous year RÖNTGEN had announced the discovery of X-rays, which were to play so important a part in atomic physics, and radiations of all known types were being eagerly investigated in the laboratories of the world. The intensity of the radiating power

of uranium compounds was measured by the rate of discharge of an electroscope in the ionized air surrounding them, and MME CURIE showed this power to be a property of the uranium atom, or of some atom closely associated with it, since it appeared to be unaffected in magnitude by the state of chemical combination of the element, and depended only on the percentage of uranium which the compound contained. With some uranium minerals anomalous results were, however, obtained, and their radiating power was found to be greater than that calculated from their uranium content. A search was therefore begun for an unknown element present in uranium minerals, but absent from pure uranium compounds, to which the extra activity could be attributed. The impurities in the minerals under investigation included compounds of barium, and when the barium was precipitated as sulphate the whole of the additional activity was found to be concentrated in the precipitate. The separation of the new element from barium proved to be difficult, and methods of fractional crystallization of the salts, such as are used in the separation of the rare earths, had to be resorted to. In this way it was possible to obtain the pure bromide of the new element: it was called *radium*.

Isolation of Radium.—The original process for the isolation of radium compounds is followed with some modifications at the present day. The uranium ore, from which insoluble impurities have been removed, is dissolved in dilute hydrochloric acid, and the barium and radium are precipitated together as sulphates. By prolonged boiling with constantly-renewed sodium carbonate solution these are converted to carbonates, which are then redissolved in hydrochloric acid. The sulphate precipitation is then repeated once or twice until all the lead and calcium have been removed. Radium chloride is less soluble than barium chloride, which itself is not very soluble, and by fractional crystallization of the chlorides the radium compound can be obtained pure; sometimes the bromides are used instead. Radium usually comes into commerce as bromide, which is always carefully dried and enclosed in sealed glass tubes.

Properties of Radium.—Whether in the metallic state or in combination, radium was found to possess properties which distinguished it from all known elements. Not only were its radiating powers enormously more powerful than those of uranium, but it gave out what appeared to be an inexhaustible supply of heat—more than a hundred calories per hour per gram of radium. Still more astonishing was the fact that the rate of evolution of heat was entirely independent of the temperature—the experiments ranged from −250° C. to 1000° C.—a result which precluded the suggestion that a chemical change of the ordinary type was taking place.

Like uranium, radium was unaffected, as regards its radiating powers, by its state of combination, and the observed facts all pointed to some internal change in the atom as the source of the phenomena.

The Radiation from Radium.—Investigation of the radiation showed that it was not homogeneous, and could be separated by the operation of a strong transverse magnetic field into three types, always denoted by the letters α, β, and γ. The α-rays were positive particles of feeble penetrating power travelling with a velocity of not more than 20,000 km. per sec., which, though very high compared with terrestrial speeds, is small compared with that of cathode rays or of light. In spite of their low velocity they were less deflected by a magnetic field than were the much faster β-rays, and this indicated a greater momentum and consequently a much greater mass. The range of the α-rays in air was less than 10 cm.
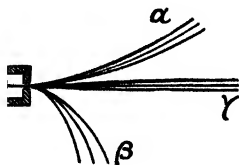
FIG. 96. THE RADIATIONS FROM RADIUM IN A MAGNETIC FIELD

The β-rays were found to be similar in every respect to cathode rays, and were in fact electrons moving with high velocity: their penetrating power, though greater than that of the α-rays, was still small. The γ-rays were unaffected by a magnetic field and were at the time of their discovery correctly supposed to be radiation of a non-material nature similar to X-rays. We now know that both γ-rays and X-rays differ from light only in their shorter wavelength; that of the γ-rays is (with the exception of MILLIKAN'S ' cosmic rays ') the shortest known for any type of radiation. Their penetrating power consequently exceeds that of the most penetrating X-rays.

The Disintegration Theory.—Further study of the α-rays revealed a fact of altogether fundamental importance to the theory of chemistry. They were shown to be identical with the positive rays produced in helium discharge tubes, and to consist of helium atoms from which two electrons had been removed. This was proved not only by measurements of the ratio of charge to mass, but also directly by Rutherford, who enclosed a radioactive substance in a very thin glass tube surrounded by an outer tube whose contents could be spectroscopically examined by passing a spark discharge through them. In blank experiments it was shown that helium in the uncharged atomic state could not leak from the inner tube to the space surrounding it. If the radioactive substance was admitted to the inner tube and the outer tube was exhausted, after some hours helium could be spectroscopically detected in

the latter: α-rays had penetrated the thin glass by virtue of their velocity and must therefore consist of charged atoms of helium. This was the first authentic proof of the disintegration of one element into another—it came rather less than a century since DALTON, in announcing the atomic theory, had stated that atoms were indivisible.

For the examination of α-rays from radioactive substances an ingenious device called the *spinthariscope* is available.   This consists merely of a screen coated with zinc sulphide or barium platino-cyanide, substances which emit flashes of light when struck by α-particles.   Under suitable conditions these flashes can be counted with a microscope, and in this way the rate of emission of α-particles from a known mass of the substance can be calculated.   If we assume that the rate of formation of helium from radium, like all other radioactive changes, follows the unimolecular law, it can be shown that radium is a comparatively stable substance: its half-life period (i.e. the period after which only half of the original quantity remains) is about sixteen centuries.   Helium can scarcely be the sole material product of radium disintegration, and still another new element was detected in very small quantity in 1900 by exposing a radium preparation to low pressure.   It is a heavy gas (its density has been directly measured with a special balance) to which the name *radium emanation* or *radon* is given.   It must be understood that the object of the reduced pressure is to remove the accumulated gas from the solid; the rate of production of emanation appears to be independent of external conditions.

Radium and the Periodic Table.—The two new elements fit without difficulty into the periodic table.   Radium has an atomic weight of 226 and an atomic number of 88; it closely resembles barium in properties and is obviously the heaviest member of Group II. The proof that radium is a true element is important, since it might otherwise be supposed that it was a helide of radon.   The distinction between radioactive disintegration and chemical change will be clearer when the structure of the atom has been considered. In emitting a helium atom with two positive charges radium has reduced the positive charge on its nucleus, and hence its atomic number, by two, so that we should expect the atomic number of radium emanation to be 86 and its atomic weight to be $226-4$ (the atomic weight of helium)$=222$.   The experimental determination of the atomic weight of emanation was very difficult, on account of the minute quantities available, and the early results varied from 220 to 223, but an examination of its chemical properties showed it to belong to the inert gas group, in which it follows xenon; its atomic number is, as anticipated, 86.

The heat produced by radium is the heat of disintegration and

can be calculated per gram-atom when once the approximate rate of disintegration is known. The calculation shows that the change $Ra \rightarrow He + RaEm$ evolves 10^{11} calories, a figure so enormously in excess of ordinary heats of reaction that it alone would be sufficient to prove that the disintegration of radium was not an ordinary chemical change. Emanation itself decays much more rapidly than radium; it emits α-particles and produces radium A, a solid element with an atomic number of $86-2=84$, which brings it into Group VI, Subgroup B, in the place below tellurium. The rate of decay of emanation can be accurately measured, since it proceeds fairly rapidly, by observing the intensity of the radiation from a fixed quantity, and has been found exactly unimolecular, which provides further evidence, if any is needed, that some internal change in the atom is taking place.

The Radioactive Series.—Radium A, though a solid substance, is usually obtained in such minute quantity as to be invisible, but can readily be detected by the intense radiation it emits; its half-life period is only three minutes. Its disintegration products are helium and radium B, which, as would be expected, is an element of the fourth group. The further disintegration of this substance into radium C is accompanied by the emission not of α-rays, but only of β- and γ-rays. If the β-ray electron has come from the nucleus, the positive nuclear charge has been increased by one unit, and the atomic number has gone up by one; instead of a displacement of two places to the left in the periodic table, such as accompanies an α-ray emission, we have a displacement of one place to the right, and radium C, with an atomic number of 83, appears to fall in the place in the fifth group allotted to bismuth.

There are obvious difficulties in the examination of the short-lived radioactive disintegration-products, and their existence is usually inferred from the shape of the disintegration-curve of the parent substance. If the product is comparatively long-lived, this will approximate to the true unimolecular shape; if it deviates, the half-life periods of the products can be calculated from the deviations. In this way a complete disintegration series of radium has been established. Radium itself is a disintegration-product, through several intermediate substances, of uranium, whose half-life period, calculated by the spinthariscope method, is about five thousand million years. If radium were not continually being produced from uranium, the supplies of radium in the world would long since have disintegrated and vanished: the great scarcity of the element is due to the rapidity of its disintegration compared with that of the parent elements. It can be shown by calculation from the unimolecular disintegration formula that in undisturbed

uranium minerals the ratio of radium to uranium ought to be a constant equal to the ratio of their half-life periods, and this is found to be correct. The ratio is about three million to one in favour of uranium, so the hope of discovering uranium minerals with large percentages of radium is illusory. Since the atomic weights of uranium and radium differ by about twelve units the intervening changes must involve the emission of three α-particles per atom. This would reduce the atomic number by $3 \times 2 = 6$, and since the actual change is only $92 - 88 = 4$, two β-ray emissions per atom must also have taken place. The immediate parent of radium was isolated in 1907; it is an element in Group IV, Subgroup A, which has been given the name *ionium*, and disintegrates into radium with the emission of an α-particle, the half-life period being about a hundred thousand years.

Element	Atomic Number	Periodic Table Group	Periodic Table Subgroup	Atomic Weight	Half-life Period	Radiation
Uranium I	92	VI	A	238	5×10^9 yr.	α
Uranium X_1	90	IV	A	234	24·5 days	β
Uranium X_2	91	V	A	234	1·14 min.	β
Uranium II	92	VI	A	234	3×10^5 yr.	α
Ionium	90	IV	A	230	$7\cdot6 \times 10^4$ yr.	α
Radium	88	II	A	226	1590 yr.	α (β)
Radium Emanation	86	O	—	222	3·8 days	α
Radium A	84	VI	B	218	3 min.	α
„ B	82	IV	B	214	27 min.	β, γ
„ C	83	V	B	214	20 min.	β, γ
„ C'	84	VI	B	214	10^{-6} sec.	α
„ D	82	IV	B	210	22 yr.	β, γ
„ E	83	V	B	210	4·85 days	β, γ
„ F (Polonium)	84	VI	B	210	135 days	α
„ G (Radium-lead)	82	IV	B	206	—	—

There is also a branch (not shown in the table) from radium C: it will be alluded to later (pp. 312, 313).

<center>THE RADIUM SERIES</center>

It will be observed that the emission of an α-particle causes a reduction of two in the atomic number and four in the atomic weight, while the element moves two groups to the left in the periodic table. The emission of a β-ray, on the other hand, leaves the atomic weight unaffected but increases the atomic number by one and causes the element to move one periodic group to the right. The explanation of these changes has already been given, but it should be noted that the β-rays emitted by radium itself do not have their origin in the nucleus and consequently do not affect the atomic number. Such secondary radiation is not a very general

phenomenon, though other examples are known. The atomic weights have been calculated by the considerations just outlined from the experimental values of uranium, radium, and radium G, which, as will shortly be shown, is a form of lead. It will also be noticed that γ radiation is always associated with the expulsion of a β-particle from the nucleus, and appears indeed to be caused by it. The chemical properties of these elements, in so far as they have been examined, are in agreement with the positions assigned to them in the periodic table.

Geiger's Law.—It is obvious that a half-life period such as 10^{-6} seconds cannot be measured by observing changes in radiation intensity. Our knowledge of such short periods is due to a relation discovered by GEIGER between the velocity of emission of an α-ray and the half-life period of the element emitting it, viz. the logarithm of the range of the α-ray (which depends on the velocity of emission) is for all elements in the same series a linear function of the logarithm of the half-life period. It is perhaps natural that rapidly disintegrating elements should emit their α-particles with high velocity, and the law has received a theoretical explanation.

The Thorium Series.—A similar series of changes is undergone by the element thorium and its disintegration-products. The activity of thorium itself is comparable with that of uranium: the facts will be found in the following table:

Element	Atomic Number	Periodic Table		Atomic Weight	Half-life Period	Radiation
		Group	Subgroup			
Thorium	90	IV	A	232	$1\cdot4 \times 10^{10}$ years	α
Mesothorium 1	88	II	A	228	6·7 years	β
,, 2	89	III	A	228	6·1 hours	β
Radiothorium	90	IV	A	228	1·9 years	α (β)
Thorium X	88	II	A	224	3·6 days	α
,, Emanation	86	O	—	220	55 sec.	α
,, A	84	VI	B	216	0·14 sec.	α
,, B	82	IV	B	212	10·6 hours	β, γ
,, C	83	V	B	212	1 hour	β
,, C'	84	VI	B	212	10^{-7} sec.	α
,, D (Thorium-lead)	82	IV	B	208	—	—

THE THORIUM SERIES

There is also a branch between Th C and Th D through an element called Th C″ (see pp. 312, 313). A third series of radioactive elements is known, including protactinium, atomic number 91, and passing through actinium, atomic number 89, and other elements, to actinium D (actinium-lead), atomic number 82, atomic weight 206, but they will not be discussed here.

Structure of the Atom.—At this stage it will be well to summarize the conclusions at which we have arrived as to the structure of atoms.

(i) An atom consists of a dense, small nucleus, positively charged, in which almost the whole of the mass of the atom is concentrated, surrounded by electrons in comparatively empty space.

(ii) The net positive charge on the nucleus is equal (in electron units) to a quantity called the atomic number, the order of the atomic numbers being nearly, but not quite, the same as the order of the atomic weights. Since the atom is electrically neutral, the atomic number is also equal to the number of electrons outside the nucleus.

(iii) If it were assumed that nuclei are composed entirely of protons and electrons, the atomic weight should be equal to the *total* number of protons in the nucleus. The fact that some atomic weights (e.g. chlorine, 35·457) deviate widely from whole numbers is a difficulty that we have not yet faced.

(iv) Nuclei of naturally occurring elements of atomic number higher than 83 display radioactivity, which consists in the expulsion of charged particles from the nucleus, accompanied by radiation of a non-material kind.

(v) Elements arranged in the order of their atomic numbers show a periodicity in their chemical properties. In the three places where the order of the atomic numbers differs from that of the atomic weights, the former is the correct order—judging by properties—and the latter is not. This fact indicates that chemical properties depend rather on atomic number than on atomic weight. The atomic number is the number of electrons outside the nucleus, and since these are the only parts of an atom with which other atoms are likely to come in contact there is nothing surprising in this conclusion.

(vi) A study of the radioactive elements appears to show that at least in this part of the table two or more elements can share the same atomic number or the same atomic weight. This conclusion is altogether contrary to the tenets of nineteenth-century chemistry, but it was verified by SODDY in 1914.

Atomic Weight of Lead.—An examination of the thorium and

radium series in the light of the periodic table suggested that the final product of each was lead. The available quantities of pure material were far too small for the direct determination to be made, but lead was found associated with both uranium minerals and thorium minerals, a circumstance which itself suggested a radioactive origin. The atomic weights of both radium and thorium were known with a satisfactory degree of accuracy, and the atomic weight of lead derived from them could readily be calculated on the disintegration hypothesis. Between radium and radium G (the hypothetical radium-lead) five α-particles are ejected per atom, so the atomic weight of the latter should be $226-5\times4=206$. Between thorium and thorium D ('thorium-lead') six α-particles are ejected per atom, so the atomic weight of lead derived from thorium should be $232\cdot1-6\times4=208\cdot1$, a difference of more than two units which should be verifiable by experiment. The determination was undertaken by SODDY in England, HÖNIGSCHMID in Vienna, and RICHARDS in America, and all the results were in agreement with theory. The highest atomic weight so far recorded for lead is $207\cdot9$, measured by Hönigschmid, using lead from a Norwegian thorium mineral; the lowest is $206\cdot0$, also measured by Hönigschmid on lead from pitchblende, a uranium mineral.

Isotopes.—The facts showed that lead could exist in two forms of different atomic weight but identical chemical properties and atomic number, and contemporary theory suggested that the atoms differed in the total number of positive charges and the total number of electrons in the nucleus, the net positive charge on the nucleus being the same for each. The atomic weight of ordinary lead is $207\cdot22$, but the closest investigation failed to detect any difference in the chemical behaviour of the three forms. Attention was also given to those elements of the radioactive series which had the same atomic number and could be obtained in quantity sufficient for investigation. Such pairs of elements were radium and mesothorium 1, both with atomic number 88, and thorium and ionium, with atomic number 90. They were shown to have identical chemical properties but different atomic weights, and for such substances Soddy proposed the name *isotopes*. They differ in properties, such as density or radioactivity, which depend on the dimensions of the nucleus, but are identical in all properties depending on the extranuclear electrons, including chemical properties, atomic volume, electrode potential, and X-ray spectrum. The possible number of isotopes with a given atomic number is by no means limited to two; lead, for example, includes not only radium G, with atomic weight 206, and thorium D (208), but also radium D (210), thorium B (212), and radium B (214). When discussing the

radium series we pointed out that there was a branch at radium C. In addition to its transformation into radium C′ by the loss of a β-particle, another change can be undergone by radium C, in which it loses an α-particle and becomes radium C″, an element with a half-life period of two minutes which disintegrates with the loss of a β-particle into radium D. It has been shown that out of 10,000 atoms of RaC disintegrating only 4 atoms lose an α-particle to give RaC″. By either route one α-particle and one β-ray are involved, and RaD (210) is the common product. Alternative transformations are not always so disparate, for 65 per cent of ThC gives ThC′ by β-ray change, and 35 per cent gives ThC″ by loss of an α-particle. The stable and inactive thorium-lead (ThD, 208) is finally produced by each route, ThC′ losing an α-particle, and ThC″ suffering a β-ray change. It is now thought that alternative behaviour of the kind shown by RaC and ThC is not conditioned by any structural difference or 'isomerism' in the nuclei, but by a difference of energy states.

The Mass-spectrograph.—Since lead, which has no radioactive properties, exists in isotopic modifications, it is reasonable to suppose that the occurrence of isotopes is not confined to the radioactive elements and will be found in other parts of the periodic table. The chemical properties of isotopes are identical, so that chemical methods of separation are useless, and since a century of atomic weight determinations had brought to light no element, with the single exception of lead and the radioactive substances, whose atomic weight was not invariable, this method of attack seemed equally unpromising. Successful *separations* of isotopes will be discussed shortly, their *detection* can be accomplished by a modification of Sir J. J. Thomson's original α-ray method (p. 297). In describing that method we mentioned that a few of the results had received no satisfactory explanation; among them was the trace of a particle in neon tubes with a ratio of mass to charge of 22. The suggestion that this was due to carbon dioxide molecules (from stop-cock grease) with a double charge $\left(\frac{44}{2}=22\right)$ was disproved by cooling the gas with liquid air, which removed the carbon dioxide particle with a single charge (44) but left the line at 22 unaffected. It was therefore suggested that this trace was due to an isotope of neon with an atomic weight 22: on this hypothesis ordinary neon, whose atomic weight is 20·183, is a mixture of isotopes of atomic weights 20 and 22, with perhaps others as well. Similar considerations could be applied to other elements, but for this purpose an apparatus was required in which the ratio of mass to charge could be determined with great accuracy. This was constructed by Aston, to whom we owe much of our knowledge of isotopes: it is

an improved form of the apparatus used by Sir J. J. Thomson and is called the *mass-spectrograph*.

The discharge tube has an aluminium cathode (earthed) with a central perforation through which stream the positive rays. The beam is reduced to a thin ribbon by two very fine slits in aluminium blocks. In order to minimize collisions between the positive rays under investigation and other gas molecules, which confuse the results, the pressure in the space between the camera and the discharge tube is kept as low as possible by means of two charcoal tubes cooled in liquid air, one connected to the camera, the other
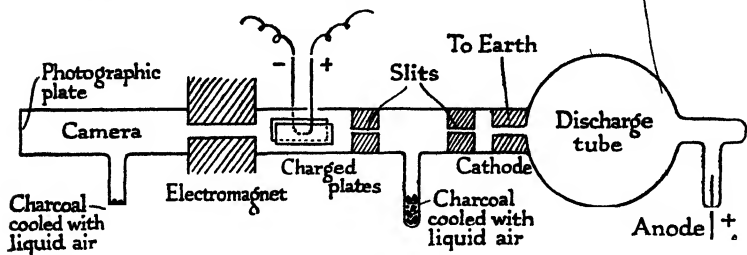
FIG. 97. ASTON'S MASS-SPECTROGRAPH (DIAGRAMMATIC)

between the slits. The discharge tube itself, after a little of a volatile compound of the element to be examined has been admitted to it, is evacuated with a mercury pump until only a trace of the contents remains. After passing the slits the beam is subjected to electric and magnetic fields, not transverse, as in Sir J. J. Thomson's apparatus, but in opposite directions. These fields produce a deviation, which can be measured from the photographic plate at the end of the apparatus, and from which the ratio of mass to charge can be calculated, with the help of the trace of a reference element such as oxygen, by a somewhat complicated procedure which we will not describe here; full details will be found in Aston's book on *Isotopes*. Different isotopes of the same element, since their positive particles have not the same masses, will clearly strike the plate in different spots.

Many metals have no sufficiently volatile compounds for use by this method. This difficulty can be overcome by fusing a salt of the metal on the anode itself, which is made of platinum foil and is strongly heated by an independent current. The positive particles obtained in this way from metallic salts are simply the particles which in solution are called ions. The necessity of using the hot anode apparatus can, however, often be avoided with the help of such substances as boron trifluoride, arsine, or iron carbonyl.

All volatile compounds are sufficiently decomposed in the discharge tube to furnish a supply of positive particles.

Results have also been obtained in America by DEMPSTER, using a mass-spectrograph of different design in which the intensities of the spots caused by different isotopes, and hence the relative abundance of each in the element, can be measured electrically. In the following table are given the latest values of the atomic weights of all the elements, together with the *mass-numbers* of all the isotopes which have been detected up to the time of writing, in the order of their abundance. The mass-number of an isotope is the nearest integer to its atomic weight. Rare isotopes are in brackets, and isotopes of the radioactive elements are not included.

ATOMIC NUMBERS, ATOMIC WEIGHTS, AND ISOTOPES

Atomic Number	Element	Symbol	Atomic Weight	Isotopes
1	Hydrogen	H	1·0080	1, (2)
2	Helium	He	4·003	4, (3)
3	Lithium	Li	6·940	7, (6)
4	Beryllium	Be	9·013	9
5	Boron	B	10·82	11, 10
6	Carbon	C	12·011	12, (13)
7	Nitrogen	N	14·008	14, (15)
8	Oxygen	O	**16·00**	16, (18, 17)
9	Fluorine	F	19·00	19
10	Neon	Ne	20·183	20, 22, (21)
11	Sodium	Na	22·991	23
12	Magnesium	Mg	24·32	24, 25, 26
13	Aluminium	Al	26·98	27
14	Silicon	Si	28·09	28, (29, 30)
15	Phosphorus	P	30·975	31
16	Sulphur	S	32·066	32, (34, 33, 36)
17	Chlorine	Cl	35·457	35, 37
18	Argon	A	39·944	40, (36, 38)
19	Potassium	K	39·100	39, (41, 40)
20	Calcium	Ca	40·08	40, (44, 42, 48, 43, 46)
21	Scandium	Sc	44·96	45
22	Titanium	Ti	47·90	48, 46, 47, 49, 50
23	Vanadium	V	50·95	51
24	Chromium	Cr	52·01	52, 53, (50, 54)
25	Manganese	Mn	54·94	55
26	Iron	Fe	55·85	56, (54, 57, 58)
27	Cobalt	Co	58·94	59, (57)
28	Nickel	Ni	58·71	58, 60, (62, 64, 61)
29	Copper	Cu	63·54	63, 65
30	Zinc	Zn	65·38	64, 66, 68, (67, 70)
31	Gallium	Ga	69·72	69, 71

Atomic Number	Element	Symbol	Atomic Weight	Isotopes
32	Germanium	Ge	72·60	74, 72, 70, 73, 76
33	Arsenic	As	74·91	75
34	Selenium	Se	78·96	80, 78, 76, 82, 77, (74)
35	Bromine	Br	79·916	79, 81
36	Krypton	Kr	83·80	84, 86, 82 and 83, (80, 78)
37	Rubidium	Rb	85·48	85, 87
38	Strontium	Sr	87·63	88, 86, 87, (84)
39	Yttrium	Y	88·92	89
40	Zirconium	Zr	91·22	90, 92, 94, 91, (96)
41	Niobium	Nb	92·91	93
42	Molybdenum	Mo	95·95	98, 96, 95, 92, 94, 97, 100
43	Technetium	Tc	(99)	
44	Ruthenium	Ru	101·1	102, 101, 104, 100, 99, 96, (98)
45	Rhodium	Rh	102·91	103, (101)
46	Palladium	Pd	106·4	106, 108, 105, 110, 104, (102)
47	Silver	Ag	107·880	107, 109
48	Cadmium	Cd	112·41	114, 112, 111, 110, 113, 116, (106, 108)
49	Indium	In	114·82	115, (113)
50	Tin	Sn	118·70	120, 118, 116, 119, 117, 124, 122, (112, 114, 115)
51	Antimony	Sb	121·76	121, 123
52	Tellurium	Te	127·61	130, 128, 126, 125, 124, (123, 122, 120)
53	Iodine	I	126·91	127
54	Xenon	Xe	131·30	132, 129, 131, 134, 136, 130, (128, 126 and 124)
55	Caesium	Cs	132·91	133
56	Barium	Ba	137·36	138, 137, 136, 135, (134, 132, 130)
57	Lanthanum	La	138·92	139
58	Cerium	Ce	140·13	140, 142, (136, 138)
59	Praseodymium	Pr	140·92	141
60	Neodymium	Nd	144·27	142, 144, 146, 143, 145, 148, 150
61	—			
62	Samarium	Sm	150·35	152, 154, 147, 149, 148, 150, (144)
63	Europium	Eu	152·0	151, 153
64	Gadolinium	Gd	157·26	158, 160, 156, 157, 155, (154, 152)
65	Terbium	Tb	158·93	159
66	Dysprosium	Dy	162·51	164, 162, 163, 161, (160 158)
67	Holmium	Ho	164·94	165
68	Erbium	Er	167·27	166, 168, 167, 170, (164, 162)
69	Thulium	Tm	168·94	169
70	Ytterbium	Yb	173·04	174, 172, 173, 171, 176, (170, 168)

Atomic Number	Element	Symbol	Atomic Weight	Isotopes
71	Lutetium	Lu	174·99	175
72	Hafnium	Hf	178·5	180, 178, 177, 179, 176, (174)
73	Tantalum	Ta	180·95	181
74	Tungsten	W	183·86	184, 186, 182, 183, (180)
75	Rhenium	Re	186·22	187, 185
76	Osmium	Os	190·2	192, 190, 189, 188, (187, 186, 184)
77	Iridium	Ir	192·2	193, 191
78	Platinum	Pt	195·09	195, 194, 196, 198, (192)
79	Gold	Au	197·0	197
80	Mercury	Hg	200·61	202, 200, 199, 201, 198, 204, (196)
81	Thallium	Tl	204·39	205, 203
82	Lead	Pb	207·21	208, 206, 207, (204)
83	Bismuth	Bi	209·00	209
90	Thorium	Th	232·05	232
92	Uranium	U	238·07	238, (235, 234)

Uses of the Mass-spectrograph.—The mass-spectrograph is now so accurate (one part in ten thousand of mass) that it is used in analysis, e.g. of the traces of impurity present in copper to be used for electrical work.   It also rivals chemical methods of atomic weight determination, and has two advantages over them: the atomic weight is determined directly, not through the equivalent, and the results are not affected by traces of impurity.   But since elements of which isotopes exist are mixtures of these isotopes in constant proportions, the relative proportions of each isotope must be known before the chemical atomic weight can be calculated from the mass-spectrograph results.   Thus if the numbers of chlorine atoms with atomic weights 34·980 and 36·978 are as a to b, the atomic weight is $\dfrac{34·980a + 36·987b}{a+b}$, and the ratio of a to b must be known before this can be evaluated.   It was at one time supposed that with the single exception of hydrogen all isotopes had integral atomic weights on the oxygen scale.   This integer was called the *mass-number*.   Recent refinements in technique have shown this to be untrue, but the atomic weights are all very close to whole numbers.   The weakest link in the calculation of atomic weights from the results of the mass-spectrograph is the measurement of the relative intensity of the spots on the photographic plate due to each isotope, but accurate results have nevertheless been obtained.   The atomic weight of beryllium was formerly given as 9·1, but the mass-spectrograph showed this element to

have no isotopes and to be of mass-number 9. Revision of the chemical method gave the value 9·02. Similarly the former value of 120·2 for the atomic weight of antimony could not be reconciled with the existence of two isotopes of mass-numbers 121 and 123 and approximately equal abundance: the new value, as determined by chemical analysis, is 121·76. Other examples could be given.

It can now be understood how it is possible for differences to occur in the order of the atomic numbers and atomic weights: how, for instance, argon can have a lower atomic number than potassium but a higher atomic weight. The isotopes of argon have mass-numbers 36, 38, and 40, but the last is so enormously more abundant that the atomic weight is 39·944. The mass-numbers of the potassium isotopes are 39, 41, and 40, but in this element the lightest isotope greatly predominates, and the atomic weight, 39·100, is considerably lower than that of argon.

Atomic Number and Atomic Weight.—The discovery of isotopes has reduced the significance of atomic weights. The most important constants of any individual atom are its mass-number and its atomic number, determining respectively its mass and its chemical properties (and to a great extent its physical properties as well). The chemical atomic weight is a statistical mean not expressing the mass of any actual atom unless no isotopes exist, and depends only on the relative proportions of the isotope mixture. It is a remarkable fact that if we exclude lead, which is unique in being partially derived from radioactive elements, there is little evidence that this proportion is not constant for all elements. We must suppose either that the isotopes of all elements have been, in the course of ages, so thoroughly mixed that it is now impossible to find any trace of local excess, or that all elements have been produced by processes which result in a mixture of isotopes in constant proportions. Even the elements present in meteorites, which probably have their origin outside the earth, have atomic weights indistinguishable from those familiar to us. Among terrestrial elements the most refined measurements, both before and after the discovery of isotopes, have failed to bring to light the smallest difference in the atomic weights of different samples. The importance of atomic weights in chemical calculations is therefore quite unaffected by recent discoveries.

Isobars.—To elements with the same mass-numbers but different atomic numbers the name *isobars* is given. An example is afforded by the most abundant isotopes of argon and calcium (mass-numbers both 40, atomic numbers 18 and 20 respectively). The ejection of a β-ray always results in an isobar, since the mass of the nucleus is thereby unaltered. To preserve the electrical neutrality of the

atom an electron must be obtained from the surroundings; it does not, however, reach the nucleus but remains in the outer parts of the atom. The ejection of an α-particle causes a reduction of two in the atomic number, and is accompanied by the loss of two electrons from the outer parts of the atom. The expulsion of a β-ray might be likened to the formation of a univalent positive ion from a metallic atom, since in both the atom loses an electron and hence acquires unit positive charge; but the processes are essentially unlike, since in the first the electron comes from the nucleus, in the second from outside it. This can be proved by examination of the products of such changes, for radioactive. elements are known which can lose electrons either as β-rays or in the formation of positive ions, but the products are not isotopic. This is one of the reasons for believing that the β-rays do come from the nucleus and not from outside it.

The isobaric isotopes have already received attention (p. 313).

Separation of Isotopes.—It is certainly a remarkable fact that lead is the only element of which naturally-occurring samples of different atomic weight are known, and these abnormal samples of radioactive origin are but a small proportion of the total supplies of the element. To separate the isotopes of other elements we have to rely on differences in properties, and apart from radioactive properties (if any) and minute differences of spectrum only density differences are available, together with properties such as rate of diffusion or evaporation which depend on density. The first attempts at separation were directed to gaseous elements whose isotopes were known to have fairly large percentage differences in mass-number and to be present in reasonable proportions—i.e. neon (20 and 22) and chlorine (35 and 37). The rate of diffusion is proportional to the square root of the molecular weight, and consequently in any one diffusion operation only a very small separation is achieved, but by long-repeated fractional diffusion Aston was able to separate neon in 1913 into two fractions of density 20·15 and 20·28, in spite of the accidental loss of the whole of the lighter fraction at an advanced stage of the work. This was the first artificial separation of an element into its isotopes; like many subsequent separations it was incomplete, but the difference was too large to be accounted for by experimental error. In the following years HARKINS in America partially separated the isotopes of chlorine by the fractional diffusion of hydrogen chloride. He passed no less than 19,000 litres of gas through the apparatus and so was able to secure highly fractionated samples in sufficient quantity to measure their density. The density of the heavier fraction was 0·1 per cent above the normal.

Another separation method which has been applied with success

*L

depends on fractional evaporation. The molecules escaping from a liquid are condensed on a glass surface cooled with liquid air and kept about a centimetre above the liquid. The lighter molecules tend to evaporate first and preponderate in the liquid condensed. BRÖNSTED and VON HEVESY applied this method to the slow evaporation of mercury at 40° to 60° in a high vacuum and obtained a density difference of one part in two thousand, and also worked on aqueous solutions of hydrogen chloride at —50°. The atomic weights of the chlorine contained in the two samples differed by 0·02. HARKINS and MORTIMER also produced a sample of mercury whose atomic weight differed by 0·189 unit from that of ordinary mercury.

Radioactive Indicators.—PANETH and VON HEVESY have worked out ingenious methods by which the radioactive isotopes, which can be detected in the minutest quantities with the electroscope, are used to indicate the presence of the inactive elements with which they were originally mixed. Thus if the soil in which a plant is growing is impregnated with a compound of lead containing a little thorium B, it is possible to follow the lead through the plant. In the same way the existence of a volatile hydride of bismuth has been inferred from the activity detected in the gas from a Marsh apparatus containing compounds of bismuth mixed with a little thorium C. If lead nitrate containing a little thorium B is dissolved in pyridine and mixed with a pyridine solution of inactive lead chloride, the isotope distributes itself impartially between the chloride and nitrate radicals when these are separated, thereby showing that a free exchange of lead ions must take place between them. This has been advanced as a confirmation of the ionic theory.

The extreme sensitiveness of the tests for these substances has been used in the determination of the solubility of the insoluble salts of lead. The weight obtained by the evaporation of a saturated solution is estimated with the electroscope.

Artificial Disintegration of the Elements.—Radioactive disintegrations cannot be accelerated by any means yet discovered, but after the nature of the disintegration process had been grasped a search was made for weapons with which to attack the nuclei of non-radioactive elements. The α-particle was the most promising, for though its velocity is less than that of the β-particle yet its momentum and kinetic energy are much greater. Elements were therefore exposed to bombardment by α-particles from a radioactive source, and the first artificial disintegration of an element was performed in 1919 by Rutherford.

The apparatus was very simple. A little radium C, the source of the α-particles, was mounted on the end of a movable rod A,

which also carried, at B, some foil of the metal to be investigated, or one of its compounds in powdered form in the case of a non-metal.   Gases could be examined by removing B and filling the chamber with the gas.   The β-rays were deflected by a magnetic field, but the positive particles traversed a window C where mica plates could be inserted of stopping power equal to a known distance in air.   The impact of the particles on a zinc sulphide screen at D was then observed with a microscope.   In more elaborate forms of the apparatus the positive rays emitted by B in other directions could be examined.
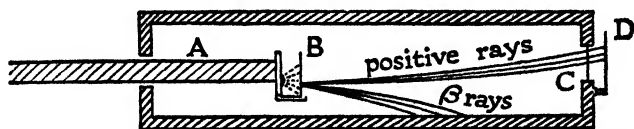
FIG. 98.   ARTIFICIAL DISINTEGRATION

The α-particles emitted by any one radioactive substance have a definite range (p. 310); about 7 cm. for radium C.   Consequently, if the chamber is evacuated and the radium C is moved farther than 7 cm. from C, no scintillations will be observed on the screen. If now hydrogen is admitted, scintillations are once more visible and the effective range is about 28 cm.   The positive particles now passing through the window are not helium nuclei (α-particles) but hydrogen nuclei with which these have collided: since the hydrogen nucleus is only about a quarter as heavy as the helium nucleus, the former acquires from the collision a velocity greater than that of the particle which strikes it.   If now the hydrogen is replaced by nitrogen, positive rays are obtained with a still greater range—about 40 cm. of air.   These are supposed to consist of hydrogen nuclei which have been detached from the nitrogen nucleus, and this has been confirmed by deflection experiments of the usual type.   The extra range of these particles as compared with those from hydrogen itself is due to the energy obtainable from the disintegration of the nitrogen nucleus, some of which is communicated to the newly-released hydrogen nucleus.   With other gases, such as oxygen, Rutherford was unable to detect any hydrogen nuclei.   The oxygen nucleus is much heavier than the helium nucleus, hence the effective range is not increased by simple collisions.   Moreover, in disintegration nearly as many positive particles are emitted backwards as forwards, but this does not occur when a nucleus is propelled as a whole.

Isotopes of Oxygen.—In 1922 BLACKETT succeeded in photographing the track of α-particles before and after collision by an

application of C. T. R. Wilson's condensation method. In this way it is possible to investigate the fate of the α-particle by which disintegration is brought about. Fig. 99 is a reproduction of a photograph taken by Blackett in nitrogen. The path of the α-particle that has suffered collision ends in a double, not a triple fork. One branch represents the hydrogen nucleus that has been expelled, the other the residue of the disintegrated atom, in which the α-particle must now be included. The nucleus of this atom has lost one positive charge with the hydrogen nucleus and gained two from the α - particle: its atomic number has therefore increased by one, while its mass-number has increased by $4-1=3$. One of the products of the disintegration of nitrogen by an α-particle would therefore appear to be an isotope of oxygen: mass - number 17, atomic number 8. For many years it was believed that oxygen had no isotopes, since the most careful search with the mass-spectrograph revealed none, but recent progress in the study of spectra has shown that oxygen does contain small quantities of isotopes. The existence of isotopes leads to doublets in the infra-red absorption spectrum, and by this means it has been shown that the oxygen isotopes have the mass-numbers 17 and 18, and are present to the extent of four parts in ten thousand and two parts in one thousand respectively. This proportion is too small to be capable of detection by the mass-spectrograph, but it involves a significant change in the ratio of the chemical atomic weights of oxygen and hydrogen. The change in this ratio is slightly more than one part in ten thousand. Isotopes of carbon and nitrogen have also been detected by the spectrum method. Like those of oxygen, they are present in very small proportions.

FIG. 99. α-PARTICLE TRACKS IN NITROGEN

Neutrons and Positrons.—Until 1930 there existed no convincing evidence that matter was composed of units other than the charged particles, electrons, and protons. It will be noted that these particles are antithetical in charge, but far from equal in mass. In that year the bombardment of beryllium compounds by α-rays demonstrated that a particle was formed (by the interaction of the α-particle with the beryllium nucleus) which, although forming no track in the Wilson cloud chamber, caused drastic nuclear reaction upon atoms at a distance from its point of origin. Detailed investigation disclosed that this new particle had no electric charge, and a mass almost equal to that of the proton. It was named the

neutron. The most recent determinations give the mass of the neutron as 1·0089, and that of the proton as 1·0076. Atomic nuclei were formerly thought to be compounded of protons and a lesser number of electrons, to correspond with the atomic number, which defined the nuclear positive charge. This view has now been abandoned, for modern investigation of nuclear properties has shown that electrons as such cannot be present in nuclei, although, of course, they appear externally as the result of radioactive disintegration. It is now accepted that if A is the mass number of an isotope of an element, $A = Z + n$, where Z, the atomic number, gives the number of protons, and n the number of neutrons. The neutron has proved a weapon of great power in the study of nuclear reactions, for its approach to a nucleus is not retarded by the violent electrostatic effects unavoidable when a-particles or accelerated protons are used for bombardment. Neutrons are now known to be ejected in a wide variety of nuclear reactions, and it is probably common knowledge that the explosive fission of the uranium isotope ^{235}U is achieved by the agency of neutrons generated in the fission itself, so that the latter becomes a ' chain ' reaction. To explain fully the course of some nuclear reactions it is necessary to postulate the emission of a particle having the small mass of the electron, but of opposite and equal charge. This particle is named the *positron.* It has usually a short existence, for on its encountering an electron both particles may disappear, and γ-radiation results. This process is another clear example of the relation of mass and energy, amounting to interchangeability, predicted by modern physical theories.

Nuclear Chemistry.—From 1896, when Becquerel discovered the natural radioactivity of certain heavy elements, until 1919 nuclear chemistry was confined to the study of the products of this type of spontaneous decay. No method was known of affecting the stability of ordinary nuclei, nor was the natural disintegration in any way controllable. A somewhat passive role was imposed on the chemists and physicists who shared the necessary investigations between them. As described above (p. 320), Rutherford in 1919 showed that atoms of nitrogen yielded protons when bombarded with a-particles, and later research proved that oxygen was simultaneously produced. Since that time the development of the subject has necessarily lain entirely in the hands of physicists, for the high-power apparatus required can only be safely operated by those specially trained in its use. On this account the subject is often called, perhaps more justly, nuclear physics, but from the systematic point of view chemistry can lay the strongest claims to include the results of these experiments, conducted by physical methods, within its own domain. It should be mentioned that in

the most recent advances of the subject, which has thereby so forcibly thrust itself on the world, chemists have played at least an equal part with their colleagues.

The ' reagents ' used to attack nuclei are as follows:

(1) *α-particles*, produced by natural radioactivity; their momenta as ejected from these sources are very high. ' Artificial ' α-particles can also be produced from helium.

(2) *Protons* or *deuterons*. These are respectively the nuclei of ordinary hydrogen (mass 1), and of ' heavy ' hydrogen or deuterium (mass 2). To secure sufficiently close approach to the nucleus under attack these positively charged particles must be accelerated by the use of powerful electric fields. Much of the recent progress in the use of these particles has depended on the building of large-scale physical apparatus (e.g. the cyclotron) to produce very large accelerations.

(3) *Neutrons*. These uncharged particles (mass 1) are obtainable only from some subsidiary reaction with charged particles. They cannot be accelerated, but can readily be slowed, if necessary, by allowing them to diffuse through matter composed of light atoms, e.g. water or graphite. ' Thermal ' neutrons are neutrons that have been so slowed that their speeds are similar to those of gas molecules at ordinary temperatures. The effect of neutrons upon nuclei is often affected by their speed.

The charged particles can, in general, only be used for attack on light nuclei, since the electrostatic repulsion of a heavy nucleus is prohibitive to close approach. Neutrons, on the contrary, can be made to react with all nuclei. Their discovery has, therefore, greatly advanced our knowledge of nuclear chemistry.

It has been found that nuclei under attack react in two ways. At the moment of impact a relatively massive particle, which may be a proton, deuteron, α-particle, or neutron, is ejected (sometimes accompanied by γ-radiation); the remaining nucleus is then usually stable. In the second kind of reaction the impinging particle is ' captured,' and the resulting nuclei of greater mass stabilize themselves rather slowly by ejection of electrons or positrons. The latter sort of reaction leads therefore to ' artificial ' radioactivity. A few of the heaviest atoms undergo, after capturing a neutron, the exceptional change of ' fission.' In this the slightly enlarged nucleus splits spontaneously into two nuclei of approximately equal mass, about half that of the parent nucleus. There may be considerable discrepancy in the summed masses of the nuclei produced and that of the parent. This difference in mass is converted into

radiation of prodigious intensity.   The most fully explored example of this kind of change is given by the equation

$$_{92}^{235}\text{U} + _{0}^{1}\text{n} = \text{atoms}_{34-57} \text{ (see below for nomenclature).}$$
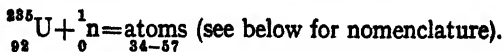
Nuclear Reactions.—In writing equations for nuclear reactions it is necessary to amplify the usual chemical symbol by adding the mass number (as superscript), and the atomic number (as subscript). The symbols used for the neutron, electron, and positron are respectively $_{0}^{1}n$, $_{-1}^{0}e$, and $_{1}^{0}e$.   In an equation it is requisite that the sum of superscripts (mass numbers) and the sum of subscripts (atomic numbers) should separately balance on the two sides.   It is also convenient to use the symbols a, p, d, and n for a-particles, protons, deuterons, and neutrons respectively.   A type of reaction can then be summarized by writing in a bracket, first the impinging particle and then the ejected particle, e.g. (p, n) means that a neutron is ejected by an impinging proton.   We shall now give, out of the many known, one example of each type of change, writing first the type of reaction, and then the equation.   Radioactive products are marked *

Type of reaction	*Equation*
(p, a)	$_{3}^{7}\text{Li} + _{1}^{1}\text{H} = 2\,_{2}^{4}\text{He}$
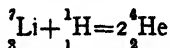
This reaction, discovered by COCKCROFT and WALTON in 1932, provided the first example of atomic fission.   The slight loss of mass in the change (concealed by the round-off atomic weights) appears as radiation.

(p, n)	$_{3}^{7}\text{Li} + _{1}^{1}\text{H} = _{4}^{7}\text{Be} + _{0}^{1}\text{n}$
(d, a)	$_{4}^{9}\text{Be} + _{1}^{2}\text{H} = _{3}^{7}\text{Li} + _{2}^{4}\text{He}$
(d, p)	$_{6}^{12}\text{C} + _{1}^{2}\text{H} = _{6}^{13}\text{C} + _{1}^{1}\text{H}$
$(d\ n)$	$_{5}^{11}\text{B} + _{1}^{2}\text{H} = _{6}^{12}\text{C} + _{0}^{1}\text{n}$
(n, a)	$_{10}^{20}\text{Ne} + _{0}^{1}\text{n} = _{8}^{17}\text{O} + _{2}^{4}\text{He}$
(n, p)	$_{12}^{24}\text{Mg} + _{0}^{1}\text{n} = _{11}^{24}\text{Na}^* + _{1}^{1}\text{H}$
(a, p)	$_{7}^{14}\text{N} + _{2}^{4}\text{He} = _{8}^{17}\text{O} + _{1}^{1}\text{H}$
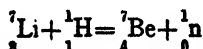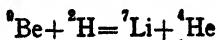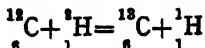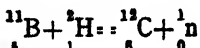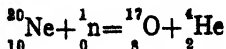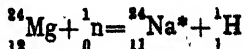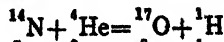
This first 'transmutation,' discovered by Rutherford in 1919, was the stimulus to all later progress in nuclear chemistry (p. 320).

(α, n) $\qquad$ $^{19}_{7}\text{F} + ^{4}_{2}\text{He} = ^{22}_{11}\text{Na}* + ^{1}_{0}\text{n}$
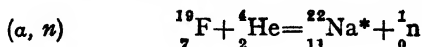
The ' artificial ' radioactivity of sodium:

$$^{24}_{11}\text{Na} \rightarrow ^{24}_{12}\text{Mg} + ^{0}_{-1}\text{e} \text{ (half-life, 15·5 hours)}$$

$$^{22}_{11}\text{Na} \rightarrow ^{22}_{10}\text{Ne} + ^{0}_{1}\text{e} \text{ (half-life, more than 6 months)}$$
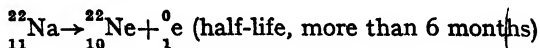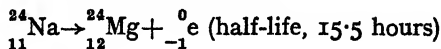
Radioactive sodium may also be obtained from ordinary sodium (used as sodium chloride) by reaction with deuterons.

(d, p) $\qquad$ $^{23}_{..}\text{Na} + ^{2}_{.}\text{H} = ^{24}_{11}\text{Na}* + ^{1}_{.}\text{H}$
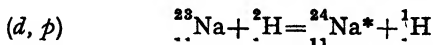
We conclude with reactions, which to chemists probably surpass in interest all others in the subject, namely the recent synthesis of the ' trans-uranium ' elements of atomic numbers 93 and greater.

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} = ^{239}_{92}\text{U}* \text{ (half-life, 23 mins.)}$$

$$^{239}_{92}\text{U} \rightarrow ^{239}_{93}\text{Np} + ^{0}_{-1}\text{e} \text{ (half-life, 2·3 days)}$$

$$^{239}_{93}\text{Np} \rightarrow ^{239}_{94}\text{Pu} + ^{0}_{-1}\text{e} \text{ (half-life, 24,360 yrs.).}$$
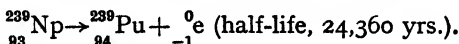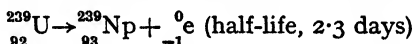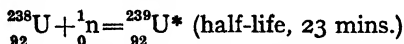
The new elements, neptunium Np, and plutonium Pu, are both radioactive, but the latter reverts, by the loss of an α-particle, to $^{235}_{92}\text{U}$ so slowly that it can be treated as a stable element.

Nuclear Stability.—An understanding of the factors involved in nuclear stability is of cardinal importance, for the relative stability must ultimately determine the abundance of atomic species, but in the absence of an accepted theory of nuclear constitution progress must be slow. One result of significance is seen when we select from the table of isotopes (p. 315) the stable atoms with only one isotopic form. These are Be 9, F 19, Na 23, Al 27, P 31, Sc 45, V 51, Mn 55, As 75, Y 89, Nb 93, Cs 133, La 139, Pr 141, Tb 159, Ho 165, Tm 169, Ta 181, Au 197, and Bi 209. Without exception all these atoms have an odd mass number A. Consultation of the table shows that with the sole exception of the lightest element beryllium, all also have an odd atomic number Z. From the relation $A = Z + n$, where n gives the number of neutrons in the nucleus, we can deduce two possibilities for odd values of A, viz.: $A =$ even $Z +$ odd n, or $A =$ odd $Z +$ even n. The fact that the second alternative almost always occurs indicates a tendency for protons (Z) and neutrons (n) to pair separately in the nucleus, this

tendency, as might be expected, being stronger for neutrons than for protons. In all the above atoms one proton must remain unpaired, while all neutrons are paired. When A is even there are again two possibilities: $A=$odd $Z+$odd n, or $A=$even $Z+$even n. In the second case all protons and neutrons are paired; in the first both a neutron and a proton remain unpaired. Inspection of the table shows how frequently even A occurs with even Z, whereas even A with odd Z is relatively rare. There does not appear to be any good evidence that helium nuclei are produced as such in the nucleus by the union of a pair of protons with a pair of neutrons. Radioactivity, 'artificial' or natural, is associated with two types of disintegrative process, or 'decay': emission of α-particles, or α-activity, emission of electrons or positrons, or β-activity. There are no known examples of the emission of protons or deuterons in radioactive transformations. The lightest element showing α-activity is bismuth ($Z=83$), and this is an activity produced artificially by bombarding bismuth with high-speed α-particles. In the β-activity of the lighter elements we doubtless see the result of a spontaneous and stabilizing change in the relative numbers of protons and neutrons, by means of the nuclear reactions.

$$\text{Proton} = \text{neutron} + \text{positron}.$$
$$\text{Neutron} = \text{proton} + \text{electron}.$$

In the example of radioactive sodium the atoms $^{24}_{11}\text{Na}$ and $^{22}_{11}\text{Na}$ are transformed respectively into $^{24}_{12}\text{Mg}$ and $^{22}_{10}\text{Ne}$; here we see the tendency to form nuclei with both A and Z even.

Mass of the Nucleus.—The theory that atomic nuclei all contain integral numbers of protons and neutrons takes us back to the views of PROUT, who more than a century ago suggested that all atoms were made up of hydrogen atoms. When the improvements in analysis showed some atomic weights to be far removed from integers his hypothesis fell into disrepute, but that difficulty has been to some extent removed by the discovery of isotopes. On the other hand the most exact measurements do show that the atomic weights on the oxygen scale of nearly all isotopes are distinguishable from integers, though they approach integral values very closely. The atomic weight of hydrogen is definitely 1·008, and if hydrogen is taken as standard the deviations of the other elements are rather greater; the oxygen standard has therefore advantages other than those originally claimed for it. The deviations themselves have been accounted for on the basis of the theory of relativity, from which it can be shown that four hydrogen nuclei closely grouped together with two electrons, as

in the helium nucleus, will have a total mass smaller than their individual masses in the free state. The difference of 0·029, i.e. $(4 \times 1·008 - 4·003)$, is in quantitative agreement with theoretical requirements.

The deviation of the atomic weight from an integer is a continuous function of the atomic number, and on these views is connected with the stability of the nucleus. In years to come it will perhaps be possible to connect nuclear stability with abundance on the earth, but at present such theories are very far from finality.

Arrangement of the Electrons.—We have hitherto concerned ourselves with the nucleus: we must now return to the question, of great importance since it determines the chemical properties, of the arrangement of the electrons in the outer parts of the atom. We have shown that these are equal in number to the atomic number and shall for a short time abandon the discussion of physical methods and revert to chemical considerations.

, Any theory of electron structure must account for the extraordinary chemical stability of the inert gases, the only elements which form no compounds. Their atomic numbers are: He 2, Ne 10, A 18, Kr 36, Xe 54, Em 86, which can also be written: 2, 2+8, 2+8+8, 2+8+8+18, 2+8+8+18+18, 2+8+8+18+18+32, and are the successive totals of the series $2(1^2+2^2+2^2+3^2+3^2+4^2)$. Since chemical combination consists in the interaction of the outermost electrons of two atoms—presumably either a sharing or an exchange—we must suppose these inert gas structures to have negligible powers of adding electrons or parting with them. It therefore seems probable that these electrons form closed groups, and that when the atomic number is one greater (as in the alkalimetals), the extra electron is the beginning of a new group. On these views the structure of the first thirteen elements will be as follows:

Element	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al
Inner Group	1	2	2	2			2	2	2	2	2	2	2
Middle Group			1	2			5	6	7	8	8	8	8
Outer Group							—	—	—	—	1	2	3

The suggested arrangement bears an obvious relation to chemical properties, and might have been predicted on that ground alone. We know that the formation of a sodium ion Na· from a sodium atom consists in the loss of an electron, and we now suspect the sodium ion to have the same electron structure as the rare gas neon. We cannot expect it to have all the properties of an inert gas, because it has an excess positive charge on the nucleus, but it does show the chemical stability which we have attributed to such a structure. In the same way a fluorine atom, by the addition of

an electron, becomes a fluorine ion, likewise with the neon electron structure but now with a deficiency of one positive charge on the nucleus. The chemical implications of these ideas will be more fully considered in the next chapter; meanwhile the physical evidence for such electron arrangements must be dealt with.

The Rutherford-Bohr Atom.—By 1913 the relation between the atomic nucleus and the surrounding electrons had been established, and it was possible for the Danish physicist BOHR to give a quantitative account of many observed phenomena on the basis of an atomic model called the Bohr, or sometimes the Rutherford-Bohr, atom. This was based on the quantum theory of PLANCK, put forward in 1900, according to which radiation can be emitted or absorbed only in units of energy equal to $h\nu$, where h is a universal constant (' Planck's constant ') and ν the frequency. These units are called quanta (see p. 272). Bohr suggested that the extra-nuclear electrons rotated round the nucleus at high speeds in closed orbits, with each of which was associated a quantum-number characteristic of the orbit. Energy could only be radiated or absorbed by the electron in quanta, and the gain or loss of a quantum caused the electron to move from one orbit to another. The quantum theory was necessary to explain the stability of the orbits or so-called stationary states, for the classical mechanics would predict a gradual loss of energy from the electron, by radiation, which would finally cause it to fall into the nucleus.

The Hydrogen Spectrum.—Bohr was able to show on theoretical grounds that for the lighter elements at least the electrons would arrange themselves in groups containing 2, 8, and 8 electrons. In each group the principal quantum-number, just alluded to, is the same: the principal quantum-number of the inner group is 1, of the next group 2, and so on. Within each group a second quantum-number expressed the eccentricity of the elliptical electronic orbit, and more recently a third and a fourth quantum-number were introduced. The great triumph of the Bohr atom was the quantitative explanation of the lines of the hydrogen spectrum. Each line represents radiation of a certain frequency and must be attributed to the transition of an electron from one orbit to another: this Bohr was able to do, thereby accounting for certain mathematical relations between the frequencies of the hydrogen spectrum lines which had previously been noted as empirical laws. The Bohr atom has also been applied with great success to other aspects of atomic physics—among them magnetic properties and the ionization of gases.

Quantum Mechanics.—In the last few years the nature of the electron has received much attention, and a new quantum mechanics has come into being, based on the mathematical work of DE

BROGLIE, SCHRÖDINGER, DIRAC, and others, according to which the electron can no longer be regarded as a point charge. It is not possible to give any description in physical terms of the nature of the electron according to this theory, which defines it mathematically. The theory leads to results in precise agreement with experiment, and offers a natural explanation of atomic stationary states. Until a new model atom has been worked out on the new basis, we shall, however, do well to continue to use the Bohr model, remembering that it is a model, in the interpretation of chemical phenomena. Just as a valency bond was used in organic chemistry as a symbol without assumptions as to its physical nature, so we may continue to speak of electronic orbits as symbols. It must not, however, be supposed that the quantum mechanics has swept the Bohr atom entirely from the field: there are still some atomic properties—the magnetic properties, for example—which receive an adequate explanation on the older basis.

Atomic Structures of the Inert Gases.—In our treatment of the Bohr atom we shall not find it necessary to go beyond the principal quantum-number. Apart from the second and third quantum-numbers, which classify the electrons inside the main groups, and the electron spin connected with the fourth quantum-number, the electron structures of the inert gases are believed to be as follows:

Gas	Principal Quantum-number				
	1	2	3	4	
He	2				
Ne	2	8			
A	2	8	8		
Kr	2	8	18	8	
Xe	2	8	18	18	
Ra Em	2	8	18	32	18	8

It will be noticed that the first two groups, 2 and 8, once built up are repeated in higher members, whereas the third group of 8 in argon has been increased to 18 by krypton. The outermost group is always 8, and a shell of eight electrons has a stability which is of great chemical significance.

SUGGESTED FOR FURTHER READING

RUTHERFORD, CHADWICK, and ELLIS: *Radiation from Radio-active Substances.*

ASTON: *Mass Spectra and Isotopes* (1942).

FRIEDLANDER and KENNEDY: *Introduction to Radio-chemistry.*

ROBERTSON: *Mass Spectrometry.*

LISTER: 'The Chemistry of the Trans-uranic Elements,' *Chem. Soc. Quart. Rev., 4.*

CHAPTER XI

THE THEORY OF VALENCY

The classical conception of valency—Valency and the periodic table—The electron-pair bond—Electrovalent and covalent binding—The electronic theory of valency—The spins of elementary particles—Illustrative examples—Problems in valency—Ionic linkages: Fajans' theory—Atomic volume and the periodic table—Effect of solvation—Covalent linkages—Conductivity of fused salts—Co-ordination compounds—The nature of electron groups and shells—The valencies of the elements Ne to A—Examples of co-ordination compounds—Chelate compounds—Stereo-isomerism—The conception of mesomerism.

The Classical Conception of Valency.—It must not be forgotten that the theory of valency embodies a quantitative principle. The valency of an element may be defined as the number of parts into which its total combining power can be divided. It follows that before we can determine the valency of an element A one or more elements of unit valency, that is of indivisible combining power, must be available. Given the univalent standards X and Y we may fix the valency of A as follows. Compounds of A with X and with Y are prepared, and from them are selected those of the forms AX_n and AY_m. It is essential that only one atom of A be present in the molecules of the compounds chosen, a matter not easily susceptible of proof unless the compounds are volatile. The valency of oxygen or sulphur in OH_2 or SH_2 is self-evident, but has been much disputed in H_2O_2 and S_2Cl_2. By suitable analysis the (integral) values n and m are determined, and these are the valencies of A in the compounds selected. The pioneers of the principle of valency, KEKULÉ and his contemporaries, instinctively chose hydrogen as their standard univalent element. In the light of modern theory we can appreciate how sure their intuition was, for hydrogen is the only absolutely univalent element, in the sense that in no circumstances can its combining power be subdivided. In their choice of chlorine as a subsidiary standard they were on less sure ground, although DUMAS had demonstrated that chlorine replaces hydrogen in organic compounds atom for atom. It was in a high degree unfortunate for early progress in the study of valency that fluorine was isolated so late in chemical history, for we know that, while a higher valency is not inconceivable, the univalency of fluorine can be trusted. MENDELEEFF strongly advocated oxygen as a (bivalent) standard element. He pointed out that if the valency of an element were assessed on the basis of its highest salt-forming oxide (basic or acidic), regularities that could not be fortuitous appeared in the

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trend of valency values over the classified elements. The main objection to the use of oxygen is that its bivalency, by introducing the possibility of more than one scheme of bonding in a given oxide, may leave the valency of the combined element ambiguous. Mendeleeff could justifiably claim that phosphorus was quinquevalent in P_2O_5, but had he known that the formula of this oxide is P_4O_{10} even in the vapour state, he might well have felt less certain.

Valencies in Periodic Groups I, II, and III.—There are sufficient elements (e.g. zinc, aluminium, mercury, oxygen) which, by their volatile compounds, exhibit their valencies unambiguously, and which also form stable ions, to prove that ionic charge (without regard to sign) is numerically equal to valency. For the majority of the elements in the above groups we have in fact to rely largely on this indirect evaluation of valency, for these elements being mainly metals form few suitable volatile compounds. It is elementary knowledge that the charges on the normal ions of these elements are not influenced by the nature of the anion: sodium is singly charged in its hydride, chloride, and oxide (Na_2O). The elements in these groups in fact commonly possess only one constant valency, although some exceptions are notable among the heavier elements, such as copper, gold, and thallium: mercury, however, is known to be bivalent in both its series of compounds. The one element in these groups readily yielding volatile compounds is boron, but its behaviour towards hydrogen is anomalous (p. 523). If we admit, as we well may, that the group (CH_3) is a good substitute for hydrogen, then we can see from the compounds $B(CH_3)_3$, BF_3, and BCl_3 that boron is in line with the other elements in respect to constancy of valency.

Valencies in Groups IV, V, VI, and VII.—The elements carbon, nitrogen, oxygen, and fluorine form an ample supply of volatile compounds, and their valencies are clearly unaffected whether we employ hydrogen or fluorine as test element. We have CF_4, (CCl_4), and CH_4; NH_3 and NF_3; OH_2 and OF_2; FH and F_2. It is interesting to note that modern electronic theory has vindicated the opinions of Kekulé, who, in his championship of the constancy of the valencies of carbon, nitrogen, and oxygen was strongly opposed by some of his contemporaries. When we turn to the heavier elements of these groups we find widely differing combining powers towards hydrogen and fluorine. For example we have PH_3 and PF_5; AsH_3 and AsF_5; SH_2 and SF_6; TeH_2 and TeF_6; IH and IF_7. If we take the simplest view about the constitution and formulae of the oxides of these elements, for example SO_3 and Cl_2O_7, they confirm the high valencies indubitably evoked by fluorine. The view most in harmony with modern knowledge of atomic structure regards these elements of Groups V to VII as exhibiting a variable combining power, with

definite minima and maxima. It is significant also that the values of the observed valencies change in steps of two units, a point noted early by chemists.

Phosphorus (3 and 5): PH_3; $PF_3(P_4O_6)$; $PF_5(P_4O_{10})$.
Sulphur (2, 4, and 6): SH_2; $SF_4(SO_2)$; SF_6, (SO_3).
Chlorine (1, 3, 5, and 7): ClH, (ClF); ClF_3; $(ClO_3)^-$; $(ClO_4)^-$, Cl_2O_7.
Iodine (1, 3, 5, and 7): IH, (ICl); ICl_3; IF_5, (I_2O_5); IF_7.

These and other examples show that hydrides exhibit the minimum valency, and fluorides and oxides the maximum. It was pointed out long ago by ABEGG that the sum of the valencies towards hydrogen and towards halogens or oxygen was always eight in Groups IV to VII inclusive; in Group IV both valencies are equal to four. He considered that hydrogen valencies, called *positive* valencies, might be of a different nature from the *negative* valencies, towards halogens and oxygen. Our present knowledge of atomic structure shows, however, that such an opinion cannot be sustained. There is no feature, for example, in the phosphorus atom prohibiting the formation of both PH_3 and PH_5 to correspond with PF_3 and PF_5. The reason why PH_5 cannot be prepared is one of energetics. The system PH_3+H_2 is very much more stable than the single molecule PH_5. Phosphorus pentachloride, PCl_5, dissociates with rise of temperature because the stability of the system PCl_3+Cl_2 is comparable to that of PCl_5. It is essentially the great stability of the hydrogen molecule H_2 that limits hydrogen valencies to the minimum possible. If therefore we re-define valency as the *maximum* number of parts into which the total combining power is divisible, we may follow Kekulé in asserting that valency is a constant, characteristic of an atom; phosphorus and sulphur, for example, are respectively quinquevalent and sexivalent elements. This conception is strongly supported by the stereochemistry of polyvalent elements. Thus the shapes of the molecules of sulphur compounds may be derived from the octahedron, some of the valencies being, of course, suppressed in the ' lower ' compounds.

The Electron-pair Bond.—Though from their introduction about 1860 single and multiple links between atoms have become the common symbols in which the chemist expresses his exhaustive and successful investigation of molecular structure, at no time before about 1916 could a conception of the nature of these links rise above the vaguest speculation. It is perhaps a sobering thought that the combination of two hydrogen atoms to form a molecule assumed by AVOGADRO in 1811 received no satisfying explanation until the year 1927. This consummation was so long delayed that those who hesitated to accept Avogadro's original hypothesis may

well be acquitted of excessive conservatism. The stimulus to put an end to this obscurantism came, of course, from physical discoveries about the constitution of the atom. About the year 1911 BOHR announced an elucidation of electronic arrangements in atoms, based firmly on spectroscopic data. At the close of 1916 KOSSEL in Europe and G. N. LEWIS in America independently showed that a satisfactory but still empirical description of the valency bond lay in the assumption that it in some way implicated a pair of electrons. Atoms entered combination when each could supply one electron of the pair, and after the chemical union each of the pair of electrons participated in the structures of the united atoms. Electron sharing was thus a mode of electron gaining. It appeared that a limit was set to this process of electron gaining in that atoms would not accumulate more than eight electrons, including those shared. This limitation became known as the *octet rule*. These early ideas proved very fertile, and with some amplifications withstood the test of application and development. The incompleteness of this theory is realized when we turn to the energetics of chemical union. As has been mentioned (Chapter VII, p. 221) all atomic combination must be exothermic. Now, if we could view all chemical union as due to a combination of ions the source of this energy of formation could be traced to simple electrostatic effects. Attempts were indeed made to implement this conception of chemical union, but when we consider such a well-known series as CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4, we see the futility of such a view, for while it is not inconceivable that carbon should be cationic in CCl_4 and anionic in CH_4, what charges are to be assigned to it in the intermediate compounds? The essential achievement of modern progress in this subject since about 1926, when quantum mechanics was founded, has been the demonstration of the source of the energy of union in what have come to be called covalent compounds, such as H_2, Cl_2, CH_4, etc. This development has at the same time confirmed the fundamental necessity for a pair of·electrons as the agency of normal, stable union, although showing that a single electron can exert bonding properties of less power. While it is in the highest degree a source of satisfaction to realize that the theory of the electron-pair bond has more than an empirical basis, the former qualitative outlook can still provide us with a valuable conspectus of chemical compounds in general.

Electrovalent and Covalent Binding.—We are now in a position to classify bonds as *electrovalent*, or *covalent*. The electrovalent bond is found in crystals such as that of sodium chloride, which is built of sodium and chloride ions, Na^+ and Cl^-. The link here does not involve an appreciable sharing of electrons, but arises almost entirely from simple, electrostatic attraction. As a consequence

the crystal is a relatively closely packed assembly of equal numbers of the ions, and the number of nearest neighbours to any ion Na^+ or Cl^- is determined not by chemical but by geometrical factors, particularly the relative diameters of the cations and anions. Electrovalent bonds are usually very strong, especially when multiply-charged ions are concerned: corundum, Al_2O_3, built of the ions Al^{3+} and O^{2-}, is nearly as hard as diamond. In a covalent link there is electron sharing. It must, however, be realized that only when the linked atoms are identical (or isotopic) is the sharing equal in respect of the two atoms. The more electronegative atom usually obtains the larger share of the bonding electrons. If it is desired to visualize the bond as the circulation of the two electrons around both nuclei, then it is to be assumed that the electrons take longer to move round the more negative atom. When the more modern view is taken that the electron charge must be 'smeared out' over all the molecule, then we must visualize the negative cloud as more dense around the more electronegative atom, the whole aspect of the molecular cloud being normally pear-shaped and not ellipsoidal; it has the latter symmetrical shape only in *homopolar* molecules, such as H_2, O_2, etc. The normal *polarity* of the covalent link comes to light in the existence (readily tested by experiment) of a definite *dipole moment*, given in value by the product of the charge displacement δ and the distance between the atomic centres r. The dipole moments of the links C—N, C—O, and C—Cl are respectively 0·4, 0·86, and 1·56 (debyes); here the increase of electronegative nature in the series of elements nitrogen, oxygen, and chlorine is well shown in the corresponding increase of dipole moment. There are among chemical links all gradations of polarity, from zero in homopolar compounds to the maximum in electrovalent links.

The Electronic Theory of Valency.—In the light of the above general principles it is seen that the valency of an element must be just the number of electrons it can share, under the condition that every electron shared brings a second into the atomic structure, up to a certain limit. For hydrogen and helium the limit is reached at only two electrons. Hence hydrogen is an absolutely univalent element, and cannot assume a higher valency (see above, p. 331). The choice of hydrogen as a valency standard by earlier chemists is thus seen as a brilliant stroke of intuition. As the limit is reached in helium before combination this element is incapable of chemical combination (when in its normal state). For the elements of the periodic series lithium to fluorine, the limit proved by both modern theory and by chemical experience is eight. Hence for these elements the 'octet' principle is quite rigidly valid. The maximum covalency shown in any compound of these elements must therefore be four. We may see this rule in operation in the

series $(BF_4)^-$, CH_4, and NH_4^+. In each of these molecules or ions the central atom, boron, carbon, or nitrogen, is covalently linked to a maximum of four univalent atoms. This series emphasizes the point that valency must depend upon electronic configuration in an atom. The electronic dispositions are identical in the species B^-, C, and N^+; we can say that these are *iso-electronic*, and naturally all have the same quadrivalency; moreover all exert the quadri-valency in tetrahedral directions.

Acting in this principle we may draw up a useful table of co-valency, not hesitating to include atomic ions.

Atomic species	Covalency				
	0	1	2	3	4
Hydrogen	H^-	H			
Lithium	Li^+	Li			
Beryllium	Be^{++}	(Be^+)	Be		
Boron		(B^+)		B	B^-
Carbon				C^-, C^+	C
Nitrogen			N^-	N	N^+
Oxygen	O^{--}	O^-	O	O^+	
Fluorine	F^-	F			

It should be clearly understood that the assignment of zero co-valency to certain ions, e.g. F^-, Li^+, etc., does not mean that they cannot form effective links; it means that these links must be ex-clusively electrovalent, and in them electron sharing is absent. Ions such as F^-, O^{2-}, O^- should strictly be classified as uni-electro-valent, non-covalent; bi-electrovalent, non-covalent; and uni-electrovalent, uni-covalent respectively. Naturally this full de-scription is burdensome and the important prefixes electro- and co-(valent) are usually omitted, and one finds a situation in which F^-, F, Na, and Na^+ are all indiscriminately called univalent. It follows from our conceptions that only those ions of covalency zero will be stable as chemical individuals: N^+ and B^- for example will exhibit as intense a chemical activity as carbon atoms.

The Spins of Elementary Particles.—Although modern theory does not permit us to adopt the simple planetary model of the motions of electrons in atoms and molecules, we must still ascribe the property of *angular momentum* to these motions. For a plane-tary orbit of an electron around an atomic nucleus, angular momen-tum would be expressed by the product Iw, where I is the moment of inertia (or ' moment of momentum '), and w is the angular velocity. It is a fundamental postulate of the quantum theory that the elec-tronic angular momentum can only have values given by the formula $\sqrt{l(l+1)}.h/2\pi$. Here h is a universal constant (Planck's con-stant), and l an integer, taking values from zero upwards. The fact that an electron can exist in an atom without orbital angular momentum

$(l=0)$ and yet not coalesce with the attracting nucleus shows how far the modern atomic dynamics has diverged from the classical form.

It has, however, proved impossible to reconcile spectroscopic data with theory unless the electron possesses another independent form of angular momentum. This second form is usually pictured as a spinning motion around its own axis. While this spin can occur in two directions it is always associated with an invariable momentum $(\sqrt{3}h/4\pi)$. Electron spin is to be regarded as an inherent electronic property, and it plays a fundamental part in theories of valency, for the two electrons implicated in a covalent bond must possess spins opposed in direction. Two atoms combine when they possess at least one each of a pair of electrons with spins so related. The occurrence of *two* electrons in a chemical bond is indeed closely bound up with the fact of electron spin. It may further be noted that the magnetic shells created by spinning electrons are the chief cause of the property of magnetism. It has recently become necessary to extend the notion of spin to the other elementary particles, the proton and the neutron, which are the units forming atomic nuclei. The latter therefore become possessed of a characteristic resultant spin. In a molecule such as hydrogen it is not necessary (at least under normal conditions) for the proton spins to have the antithetical relation rigorously imposed on the two electrons forming the bond. Two forms of hydrogen molecule are thus possible, according as the proton spins are ' parallel ' or ' anti-parallel.' Since these forms, known respectively as ortho-hydrogen (parallel spins) and para-hydrogen, differ slightly in energy, each may be regarded as a special type of allotrope (see further, p. 362).

Illustrative Examples of the Electronic Theory.—Guided now by the classical principle of valency saturation the reader will find no difficulty in assembling the above atomic species into known molecules and ions. Thus ' hydrogen ion ' H_3O^+ and ammonia NH_3 are seen to be isoelectronic and structurally analogous; both are pyramidal in shape. As an illustrative exercise in the use of the table we may set out and discuss the possible formulae of all the ions formed by the union of nitrogen and oxygen:
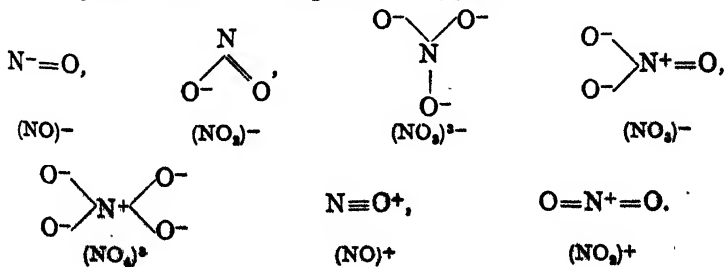
In these formulae the net charge shown is the algebraic sum of those on individual atoms. The nitrite ion NO^-_2 and the nitrate ion NO^-_3 will be familiar. The cation NO^+ occurs in lead-chamber crystals (p. 686), and in salts such as nitrosyl perchlorate, $NO.ClO_4$. The nitronium ion NO_2^+ is present in concentrated nitric acid, and is responsible for aromatic nitration (p. 125). The anion NO^- appears to be unstable, and spontaneously condenses, with some rearrangement, to the hyponitrite ion $O^-\!\!-\!N\!\!=\!\!N\!\!-\!\!O^-$. As the ortho-carbonate group is well known in organic ortho-carbonic esters, e.g. $(C_2H_5O)_4C$, the ortho-anions $(CO_4)^{4-}$, $(NO_4)^{3-}$, and $(NO_3)^{3-}$ might have been expected to have stable existence. All, however, readily undergo hydrolysis (see p. 341):

$$(NO_3)^{3-}+H_2O=(NO_2)^-+2OH^-,$$
$$(NO_4)^{3-}+H_2O=(NO_3)^-+2OH^-,$$
$$(CO_4)^{4-}+H_2O=(CO_3)^{2-}+2OH^-,$$
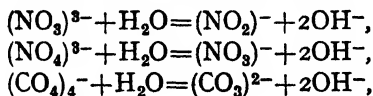
yielting respectively the normal carbonate ion $O\!\!=\!\!C\!\!\begin{smallmatrix}O^-\\O^-\end{smallmatrix}$ and the

nitrate and nitrite ions shown above. Anticipating some later considerations, we may remark that the ortho-phosphate ion $(PO_4)^{3-}$ differs from the hypothetical ortho-nitrate ion $(NO_4)^3$ structure, because phosphorus can be truly quinquevalent, that is, it can accumulate 10 electrons in its outer shell.

The ortho-phosphate ion is resistant to hydrolysis in solution, and must be assigned the formula

$$\begin{smallmatrix}O^-\\O^-\\O^-\end{smallmatrix}\!\!\!\!>\!\!P\!\!=\!\!O$$
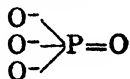
The anion $(BO_3)^{3-}$ derived from the tervalent element boron and analogous to $(NO_3)^{3-}$ is well known in crystals. In aqueous solution, however, it is readily hydrolysed first to the simple anion $(BO_2)^-$:

$$(BO_3)^{3-}+H_2O=(BO_2)^-+2OH^-,$$
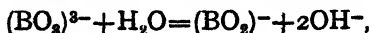
which is analogous to the nitrite ion, and then these simple anions tend to condense into larger groups by sharing (neutral) oxygen:
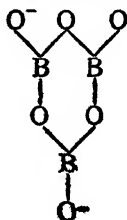
Thus potassium metaborate is $K_3B_3O_6$, and not KBO_2, as is sometimes written. The ortho-nitrate ion $(NO_3)^{3-}$ is susceptible to hydrolysis and cannot exist in aqueous solution; but, unlike metaborate ion, the nitrite ion shows no tendency to polymerize.

Typical Problems in Valency.—It is by their power to solve difficult chemical problems that new theories will most impress the chemist. As an illustration we will consider the compounds carbon monoxide, nitric oxide, and ozone. The first two of these molecules present obvious and grave valency problems. Four bonds between carbon and oxygen are excluded on stereochemical grounds; on the other hand, carbon monoxide shows none of the properties to be expected in a compound of bivalent carbon; it combines with halogens only under the stimulus of catalysts and at temperatures above normal; it manifests no tendency to polymerize. Glancing at the table on p. 336 we see that C^- would saturate O^+, both being tervalent, and the resulting molecule would be electrically neutral. The structure $C^- \equiv O^+$ would, as LANGMUIR pointed out years ago, be closely analogous to (and iso-electronic with) the molecule of elementary nitrogen, $N \equiv N$, and it is not surprising that the physical properties of the two molecules (b.pt., critical constants, etc.) are almost equal. It must be noted that since oxygen is much more electronegative than carbon the six electrons involved in the triple bond, although all shared, will not be equally shared, and the accumulation of charge density round the oxygen will offset the strong polar effect due to the ionic charges. In this particular case the two effects happen to be almost equal, and, as has been fully established, carbon monoxide is almost non-polar (see further, p. 354).

Nitric oxide clearly lies between the structures $N^- = O$ and $N \equiv O^+$ already mentioned (p. 337). We assign it the formula $N \equiv\!\!\!\equiv O$, wherein the broken line means a single-electron bond, or in more nearly classical terminology, a half-bond. With the six unshared electrons the five bonding electrons complete the total of eleven valency electrons derived from the original atoms, and both atoms complete their ' octets.' It has already been observed (p. 334) that modern theory allows bonding power to a single shared electron. The physical properties of nitric oxide are completely in agreement with this ' $2\frac{1}{2}$ '-bond formulation (for another treatment of nitric oxide, see p. 354).

Ozone presents a problem of a different nature, for on purely chemical grounds the classical formula

is not unsatisfactory. A detailed study by physical methods that cannot be described here proves conclusively that the angle between the bonds cannot be 60° as required by the formula above, but is near to 120°. When we propose the alternative formula, $O^-\!-\!O^+\!=\!O$, we solve this difficulty, for it is well known from studies of the stereochemistry of carbon compounds that the angle between a single bond and a double bond is 125° (see further, p. 352).

It has long been known that when the alkali metals sodium and potassium are freely oxidized in oxygen the oxides Na_2O_2 and KO_2 (formerly wrongly written K_2O_4) are produced in preference to those expected on simple valency grounds, viz. Na_2O and K_2O. Sodium peroxide and potassium superoxide KO_2 have been shown (by methods of X-ray diffraction) to contain the ions $(O_2)^=$ and $(O_2)^-$ respectively. The first anion is easily formulated as $(O^-\!-\!O^-)$, but the second is more obscure. Just as we assumed that nitric oxide lay between $N^-\!=\!O$ and $N\!\equiv\!O^+$, so $(O_2)^-$ lies between $O\!=\!O$ and $O^-\!-\!O^-$, and its formula is to be written $(O\!=\!O)^-$, where the broken line again means a single-electron bond. The three electrons in the bond with the ten unshared make up the total of thirteen electrons from the two oxygen atoms with the single charge added. The molecule NO and the ion O_2^- are among the rare examples of ' odd electron ' structures. Whenever possible 2-electron bonds are always formed, so that most of the known chemical compounds have an even total number of electrons, as was first pointed out by G. N. Lewis in support of his original theory.

Ionic Linkages: Fajans' Theory.—What determines the nature of the bond between the atoms of a compound? Why is it that sodium chloride is a solid with high melting-point and ionic lattice, fully ionized in the solid state and in solution, while carbon tetrachloride is a volatile liquid immiscible with water and in which no trace of ionization can be detected? To say that sodium chloride is ionic and carbon tetrachloride covalent is merely to state the problem in other terms, but an answer, if only a partial one, can be given. According to FAJANS, the formation of ionic links is promoted by a high atomic volume [1] for the cation as compared with the anion, and by small ionic charges. It is obvious that the larger a metallic atom the less tenaciously will the outer electrons be held by the nuclear charge. The formation of a cation ought therefore to be assisted by a large atomic volume, while from similar reasoning it follows that for the production of anions a small atomic volume is desirable. It is likewise clear that when several electrons are to be removed from an atom the difficulty of doing so will progressively increase, for the removal of each one increases the residual positive charge by which the

[1] The atomic volume is the atomic weight divided by the density

others are retained. The formation of multiply-charged anions is particularly difficult, because an electron separated from such an anion still leaves it negatively charged and hence with no great power of recovering the electron. Thus the charge of elementary ions goes up to four for cations (e.g. $Sn^{····}$), but only up to two for anions (e.g. S''), and even doubly-charged anions show a tendency to reduce their charge by reaction with water:

$$S''+H_2O \rightleftharpoons OH'+HS'. \quad O''+H_2O \rightarrow 2OH'.$$
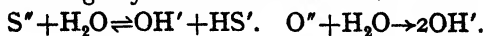
Many examples of these ideas may be given. In any periodic subgroup the metallic character increases with increasing atomic number, and the most electropositive of all metals are the alkali-metals, which form 'univalent' ions. Thus in the periodic table metallic character increases from right to left and from top to bottom—e.g. in the order K, Rb, Cs; or As, Sb, Bi; or Ti, Sc, Ca, K. In the halides the fluorides are often ionic when the other halides are covalent—e.g. AlF_3 compared with $AlCl_3$, or HgF_2 compared with $HgCl_2$. After protracted speculation about it, the heaviest
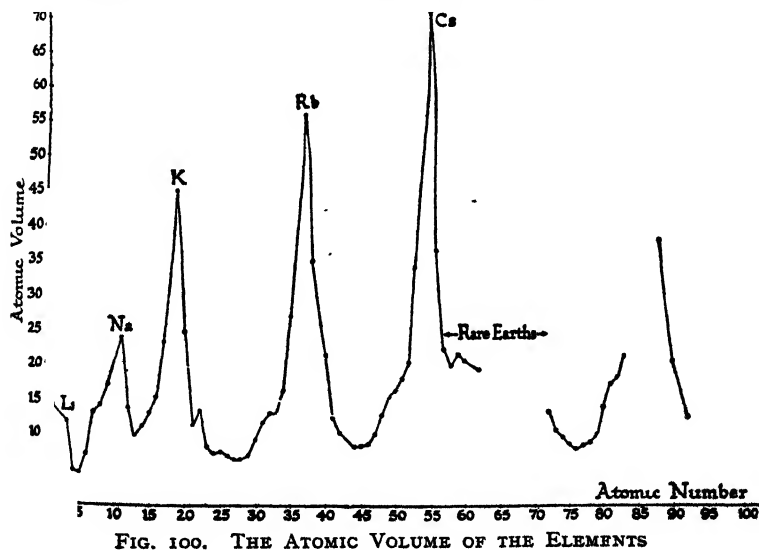
FIG. 100. THE ATOMIC VOLUME OF THE ELEMENTS

'halogen' (at. no. 85, astatine, At) appears at last to have been isolated, as an isotope of mass no. 211, obtained from the nuclear reaction $Bi(a, 2n)At$. The half-life of this isotope is only 7·5 hours but in spite of this handicap it has been found that astatine occurs in solution not only as the anion At^- but as cations in at least two
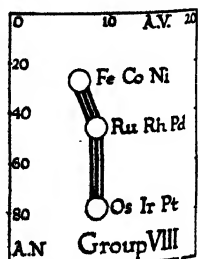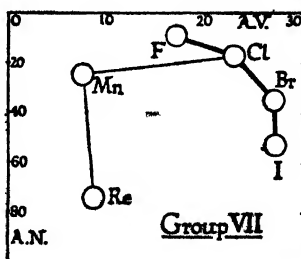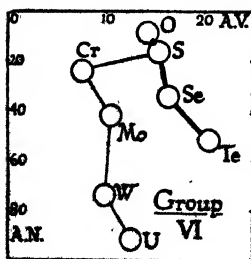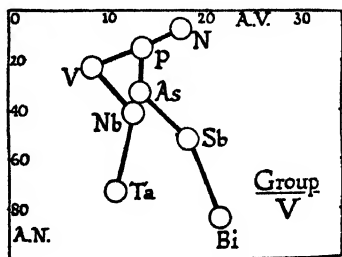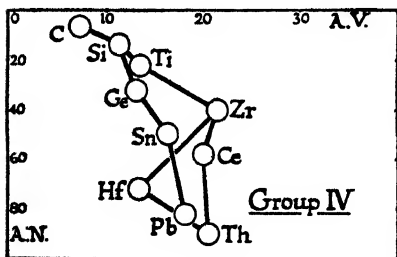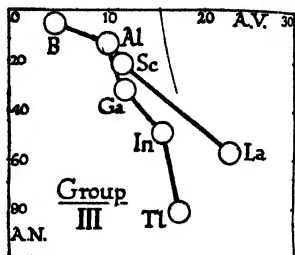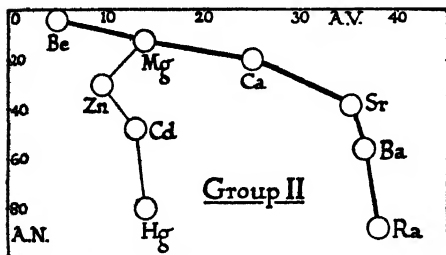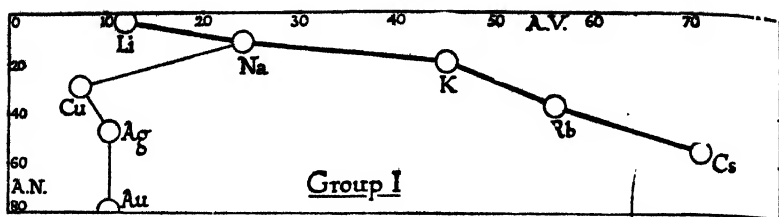
FIG. 101. THE PERIODIC GROUPS AND ATOMIC VOLUME (ATOMIC VOLUME PLOTTED AGAINST ATOMIC NUMBER)

oxidation states, and the element can be deposited at the cathode. It is therefore apparent that the tendency to metallic properties is evinced even in the most electro-negative group of elements.

Atomic Volume and the Periodic Table.—The extreme importance of atomic volume in determining the chemistry of an element has only recently been recognized, but many years ago LOTHAR MEYER showed that this was one of the most unmistakably periodic of the atomic properties. In Fig. 100 the atomic volume is plotted against the atomic number: the peaks of the curve are occupied by the alkali-metals. It is still more instructive to join up the points representing elements in the same group, as has been done in the small diagrams of Fig. 101. This shows that in Groups I and II the atomic volumes of Subgroup A fall in a natural sequence with those of the typical elements, while in Groups VI and VII the typical elements go with Subgroup B: in Groups III, IV, and V there is little to choose between them. This is in excellent agreement with what is known of the sequence of other properties: it will also be noticed that the differences between the subgroups are extreme at the ends of the table but decrease towards the middle. The atomic volumes of the Group VIII metals are all very close. Where elements exist in allotropic forms, the lowest value of the atomic volume has been taken: for elements gaseous at ordinary temperatures the figures refer to the liquid at the boiling-point. The inert gases have been omitted.

Effect of Solvation.—It is never prudent to suppose that because a compound in the pure state is covalent it will continue to be so when in solution. The hydration that it may undergo in water may profoundly alter its properties, and this is true of other solvents as well. Pure hydrogen chloride is covalent, but dissolved in water it is highly ionized: the ions are not H˙ and Cl′ but (H_3O^+) and Cl′. The increase in ionic character may again be connected with increase in the size of the cation. This reaction with the solvent is of fundamental importance in the study of acidity, and hydrogen chloride is a strong acid only in solvents in which it is solvated. The same applies to nitric acid, which is covalent even in such solvents as alcohol. The dielectric constant of the solvent, as was shown in Chapter IV, is of less importance. Of all known acids, perchloric acid best preserves its ionic character in non-aqueous solutions. This points to a small volume for the perchlorate ion (i.e. small solvation), and is in harmony with the exceptionally high mobility of the ion in alcoholic solution. Organic acids, on the contrary, have large anions, and with few exceptions are predominantly covalent.

Covalent Linkages.—Covalent compounds are distinguished by the absence of ionization in ionizing solvents, though, as already
M

mentioned, solvation may turn them into ionic compounds. The absence of ions may be proved by the usual chemical tests, by low electrical conductivity, and in many other ways. In comparison with ionic compounds of similar type covalent substances are marked by volatility and solubility in non-ionizing solvents (usually organic) such as benzene or chloroform. Covalent compounds often have an elaborate crystal lattice of non-ionic type, whereas in the crystals of ionic compounds the dominant principle often seems to be the packing of the ions together in the smallest possible space, some form of cubic lattice being very common.

As an example of compounds of similar formula, one ionic and the other largely covalent, we may give the fluoride and bromide of aluminium:

Aluminium Fluoride (Ionic)	*Aluminium Bromide (Covalent)*
Melts at 1000°	Boils at 270°
One form is insoluble in water: others are slightly soluble. The solutions are ionized.	Very soluble in water: the solutions are hydrolysed.
Insoluble in organic liquids.	Markedly soluble in organic liquids (e.g. benzene): the solutions are not ionized.

Conductivity of Fused Salts.—The electrical conductivity of the fused salt is one of the criteria for covalency. The following table shows the conductivities at the melting-point of the chlorides of some of the elements in the earlier groups of the periodic table, expressed in the same units:

HCl less than 10^{-6}.

LiCl 166, NaCl 133, KCl 103, RbCl 78, CsCl 67.

BeCl$_2$ ·09, MgCl$_2$ 29,	CaCl$_2$ 52, SrCl$_2$ 56, BaCl$_2$ 65. HgCl$_2$ $2 \cdot 5 \times 10^{-5}$ (Hg$_2$Cl$_2$ 40).
BCl$_3$ 0, AlCl$_3$ $1 \cdot 5 \times 10^{-6}$,	ScCl$_3$ 15, YCl$_3$ 9·5, LaCl$_3$ 29·0. InCl$_3$ 15 (InCl$_2$ 29, InCl 130), TlCl$_3$ less than $2 \cdot 5 \times 10^{-4}$ (TlCl 47).
CCl$_4$ 0, SiCl$_4$ 0,	SnCl$_4$ 0 (SnCl$_2$ 22).

It has further been found that the variation with temperature of the conductivity of the fused alkali-metal chlorides is equal to the variation with temperature of the viscosity, so it is supposed that these chlorides are fully dissociated in the fused state. It is very interesting to notice that the mobilities of the alkali-metal ions decrease, as one would expect, as the atomic volume increases, whereas in aqueous solution the mobility of the hydrated ions increases from lithium to caesium (p. 153). In other groups

the dissociation is probably not complete, and the increase in dissociation as the cation grows larger is of more effect than the accompanying decrease in mobility: Group II, typical elements and Subgroup A, is an excellent example of this. It should be noticed, too, how the tendency to covalency increases in Groups I to IV: the higher the valency of the cation the less its power of forming an electrovalent bond. This effect is also strikingly brought out in the chlorides of elements of variable valency, such as indium, thallium, and tin, the chlorides of lower valency having a pronounced conductivity even when the chloride of highest valency has none.

The occurrence of isomerism is naturally an unmistakable sign of the existence of covalent bonds, since ionic bonds have not the fixed orientation necessary to it. Co-ordinate links (below) may also serve as a basis of isomerism.

Co-ordination Compounds.—Another branch of chemistry wherein the new theories have proved their power is that of the so-called ' molecular compounds.' It has long been known that many metallic salts will absorb and combine with ammonia: for example, cupric sulphate yields a deep blue compound, $CuSO_4.4NH_3$, and silver chloride, $AgCl.2NH_3$; nickel sulphate yields $NiSO_4.6NH_3$. Before the foundation of the electronic theory it had become clear, mainly as the result of experiments by WERNER, that in the very numerous compounds of this class the ammonia is bound wholly to the metallic ion. When we remember that a nitrogen atom possesses five valency electrons it can be seen that in ammonia NH_3 a total of eight valency electrons in all is present, but only six are shared to bind the three atoms of hydrogen. We have but to assume that each of the pairs unoccupied in free ammonia is employed to build up a new shell round the cupric ion Cu^{++} to form a conception for the reason of the union.
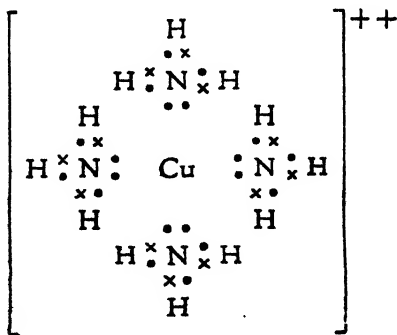
A covalent linkage formed by this unilateral sort of electronic transaction is often termed a *co-ordinate linkage*, because Werner chose the term *co-ordination compound* for the type of molecular compound we are discussing. It must not be assumed that the linkage once formed differs in any way, certainly not in stability, from an ordinary covalent link. If we pursue this explanation over the whole wide field of known co-ordination compounds we shall often find that the octet rule must be abandoned. Thus in the familiar ferrocyanides and ferricyanides we find six CN^- groups bound to the ferrous or ferric ion, and in the recently prepared molybdeno-cyanides there are eight CN^- groups round a molybdenum ion. This brings us again to the question whether, as was formerly thought, the octet rule is universal. That it is rigorous for the light elements from lithium to fluorine is certain, but much chemical evidence would have to be discredited if it were not to be relaxed for heavier elements. The well-known structures, $(SiF_6)^{2-}$, SF_6, and $(PCl_6)^-$ (recently demonstrated in solid phosphorus pentachloride), seem to suggest that twelve electrons can be accommodated round the nuclei of these atoms. While this question cannot be regarded as completely settled, most opinion favours the abandonment of the octet principle for elements after fluorine (see further, p. 348). Compounds like ammonia with unshared electrons are very numerous, and a vast range of co-ordination compounds is known in which anions (e.g. Cl^-, SO_3^{2-}, $C_2O_4^{2-}$, NO_2^-, CN^-, etc.) and neutral molecules (e.g. NH_3, H_2O, CO, NO, etc.) act as ' donor ' groups, that is, supply one or more pairs of electrons towards the shell built up round a central atom or ion. The best-known and perhaps most important class has a central atom or cation of the metals of the mid-portion of the ' long ' series in the periodic system. It has become customary to symbolize a co-ordinate link by the sign →, the arrow-head pointing *away* from the 'donor' group or ion. This convention is useful, provided it is not assumed to mean that a co-ordinate link differs in nature from an ordinary single bond, where the arrow-head would not be used.

The General Nature of Electron Groups and Shells.—In order to realize fully the contribution that modern theory can make to the interpretation of chemical valency, it is necessary to consider the nature and particularly the maximum possible electronic content of atomic shells. The theory of quantum mechanics, developed since about 1927, now provides an orderly conspectus of atomic structure, and its predictions are found to be in complete harmony with long-established facts brought to light by the study of atomic spectra. For our purposes we shall define an atomic *group* as a set of electrons bound to the nucleus by forces of similar magnitude. This description (as will shortly appear) differs some-

what from the spectroscopic and quantum-mechanical classification, but in chemical changes it is principally the energy of electronic binding in atoms that determines how they combine.

$$
\begin{array}{lllll}
 & & & & \text{IV} \\
 & & & \text{III} & \\
 & & \text{II} & M\ (18) & N\ (32) \\
 & & L\ (8) & 3p\ (6) & 4p\ (6)\ldots 4d\ (10) \\
I & & 2p\ (6) & 3s\ (2)\ \ldots\ldots 4s\ (2)\ldots 4f\ (14) \\
K\ (2) & & 2s\ (2) & [\text{Na}-\text{A}] & 3d\ (10) \\
1s & & [\text{Li}-\text{Ne}] & & [\text{K}-\text{Kr}] \\
[\text{H, He}] & & & &
\end{array}
$$
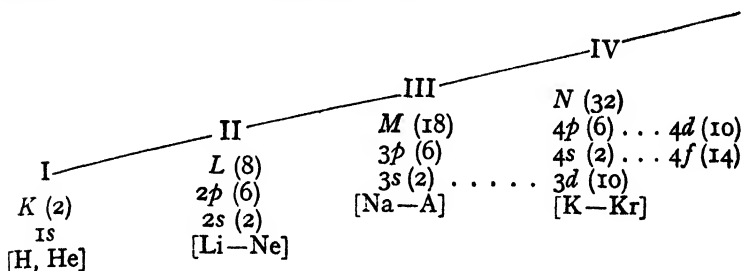
In the above scheme an attempt has been made to include not only the spectroscopic terminology and classification, but also the energy separation of the various electronic classes. The capital letters K, L, M, N, etc., designate *shells* of electrons whose behaviour is associated with a given 'quantum-number,' 1, 2, 3, 4, etc. The meaning of the term 'quantum-number' is to be sought in the equations of quantum mechanics, and it is unnecessary to elaborate its interpretation here. It will be seen that the total possible electronic content of a shell with quantum-number n is $2n^2$, giving the numbers 2, 8, 18, 32, and so on. The small letters s, p, d, f, designating sub-shells, are drawn from spectroscopic terminology, and are taken to indicate types of electronic orbit differing in angular momentum, as described on p. 336.

Type of orbit	l (see p. 336)	Angular momentum of electron
s	0	0
p	1	$\sqrt{2}.h/2\pi$
d	2	$\sqrt{6}.h/2\pi$
f	3	$2\sqrt{3}.h/2\pi$

The numerals in parentheses after the small letters give the maximum number of electrons allowed to adopt the type of motion concerned. It will be seen that these numbers follow the integral sequence $2(2l+1)$.

The difference in binding energy is largest between shells K and L, and steadily decreases in the order $K.. N....$ To assess the order of magnitude of the energy difference between the K and L shells, we may note that if all the ($1s$) electrons in a gram-atom of hydrogen were to be transferred to the L shell an input of about 250,000 calories would be needed. It is this enormous energy difference which confines hydrogen to univalent behaviour, for

while two electrons may be accommodated in the K shell, further electrons entering the atom as a consequence of higher covalency, must pass to the L shell, and no known terrestrial chemical reaction could supply 250,000 calories per atom combining. Owing to its minimal nuclear charge the energy difference between K and L shells is less in hydrogen than in any other atom.

In the K and L shells the *shell* and the *group* (as defined above) coincide, for there is only a comparatively small difference in binding energy between s and p types in any shell. On the contrary, there is usually a large difference between s (or p) and d (or f). For this reason the sub-shell $3d$ falls not into Group III but into Group IV, while electrons in $4d$ and $4f$ fall into Group V (not completely shown in the diagram). This complication leads directly to the appearance in the Periodic System of its typical ' long ' periods (filling of d orbits, see p. 772), and of the rare-earth elements in their assigned position (filling of $4f$ orbits, see p. 542). It will be convenient to remember that a filled electron group contains s and p electrons of quantum number equal to the group number, and d (and f) electrons of quantum number one less than the group number; in short, Group n contains two ns and six np electrons, with ten $(n-1)d$ electrons: Group V also has fourteen $4f$ electrons. Electrons cannot adopt a p type of orbit if the quantum number is less than 2, nor d or f types if it is less than 3 or 4 respectively.

The Valencies of the Elements Ne to A.—In neon $(Z=10)$ the shells K and L (identical with Groups I and II) are completed, while in argon $(Z=18)$ the third group is full, but the M shell still lacks its complement of ten $3d$ electrons, notwithstanding the inertness of argon. We might deduce from these facts that the valencies of the active intermediate elements Na to Cl would be governed by the same deficiencies in the s and p classes alone, as certainly determine the valencies of the set of elements Li to F. In short, we might assert an ' octet principle ' for the Periodic Series 3, as we do, in complete accord with chemical facts, for Series 2. We should then be compelled to devise structures for the compounds of e.g. phosphorus, sulphur, and chlorine, which showed no more than an octet of electrons associated with these atoms. For example, we could write for ions of the type $(XO_4)^{n-}$ the structures

$$O \uparrow \\ O \leftarrow P^{3-} \rightarrow O \qquad (PO_4)^3 \\ \downarrow \\ O$$

$$O \uparrow \\ O \leftarrow S^{2-} \rightarrow O \qquad (SO_4)^2 \\ \downarrow \\ O$$

$$O \uparrow \\ O \leftarrow Cl^- \rightarrow O \qquad (ClO_4) \\ \downarrow \\ O$$
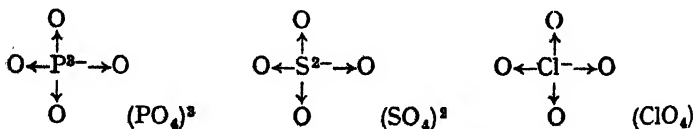
By the lavish use of ' co-ordinate ' linkages so exemplified it proved feasible to account theoretically for many of the compounds

concerned. With the accumulation of detailed knowledge of molecular structure drawn from the modern methods of X-ray and electron diffraction, however, it has become increasingly difficult, and not infrequently impossible, to justify such structures. The co-ordinate link is essentially a single bond, but the known dimensions of e.g. the sulphate ion appear to demand bonds between sulphur and oxygen at least as short as double bonds. The striking fact, mentioned on p. 333, that the valencies of these elements advance to a maximum as wholly even or wholly odd numbers can hardly be fortuitous, and is exactly predictable if we assume that the electrons occurring in pairs in the $3s$ and $3p$ sets can be unpaired by spontaneous transference (or ' promotion ') to vacant $3d$ orbits: each pair of electrons so separated must increase the valency by two units.

The indications are that valency electrons in phosphorus, sulphur, and chlorine can utilize the $3d$ orbits, even though these belong (by energetics) to Group IV. The difficulty is to explain why a similar means of chemical activation does not take place with argon. At present therefore we have a contradictory state of affairs. The sequence of elements in the Periodic System is in harmony with our classification into *groups*, while the detailed valencies of the elements appear to require us to ignore the energetic distinction between groups and shells. It is to be hoped that further advances will succeed in resolving these difficulties.

Some Examples of Co-ordination Compounds.—The electronic theory accounts successfully for the types of valency met with in co-ordinated compounds. In our discussion of complex ions (p. 201) we showed that from platinous chloride, $PtCl_2$, ammonia, and potassium chloride the following complex ions could be obtained:

$$(Pt.4NH_3)\text{''} \quad (Pt.3NH_3.Cl)\text{'} \quad (Pt.NH_3.Cl_3)\text{'} \quad (PtCl_4)\text{''}$$
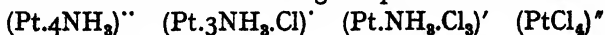
as well as an unionized substance, $Pt.2NH_3.Cl_2$. It is now clear that in these compounds the ammonia molecule replaces a chlorine ion by virtue of its donor properties. The electron structures of the unionized $Pt.2NH_3.Cl_2$ and of $(Pt.NH_3.Cl_3)\text{'}$ are:

A further proof of the covalent nature of the linkages in these compounds is afforded by the existence of isomerism. Thus $Pt.2NH_3.Cl_2$ exists in two isomeric forms, which leads one to suppose that the groups are arranged not in a tetrahedron, as in the carbon compounds, since on this basis no isomerism would be possible, but in some less symmetrical manner—in a plane.
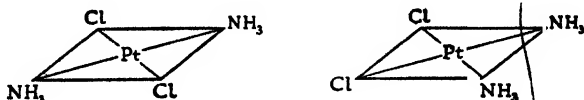
In the numerous compounds in which not four, but six groups or atoms are connected by covalencies or co-ordinate valencies with the central atom, an octahedral arrangement obtains. Thus platinic chloride, $PtCl_4$, forms with ammonia an unionized compound, $Pt.2NH_3.Cl_4$, which occurs in two forms to which we may assign the structures:
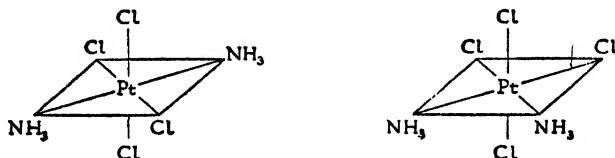
The student should assure himself by turning the diagrams round (1) that the structures really are different, and (2) that no others are possible. The elements of Group VIII are particularly liable to form such compounds, and the same applies to chromium.

Inner Complex Salts.—Most interesting examples of internal co-ordination in what are called *chelate* compounds have been much studied in recent years. In these compounds a metallic atom
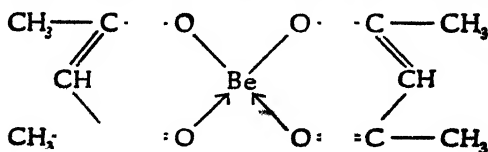
which might be expected to appear as an ion does not do so; the compounds are unionized, frequently volatile, and show every symptom of covalency. They contain rings in which the metallic atom is bound by co-ordination with one or more other atoms in the same molecule, and the property is therefore very readily exhibited by β-diketones, such as acetylacetone, which contain

suitably placed oxygen atoms.   Acetylacetone in the enolic form is $CH_3.C(OH):CH.CO.CH_3$, and the hydroxylic hydrogen atom is acidic and can be replaced by metals.   The diagram shows the structure of the beryllium derivative of acetylacetone, the arrows indicate a co-ordinate link in which an oxygen atom provides and the beryllium atom accepts a pair of electrons.   The beryllium atom has its octet complete and the compound is completely covalent. A similar explanation has been advanced of the complexes produced from metallic ions and hydroxylic organic substances—see, for example, Fehling's solution (p. 461).

Stereo-isomerism.—It has been abundantly proved that in favourable circumstances the presence of these chelate groups may lead to stereo-isomerism.   In the metallic ammines the stereo-isomeric

A   B   C
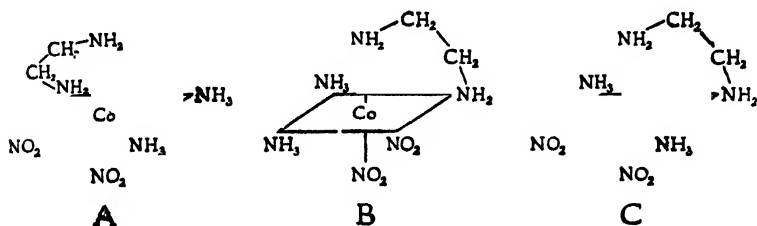
compounds which have been most investigated are those containing ethylene diamine, $NH_2.CH_2.CH_2.NH_2$.   The amino group, $-NH_2$, has the same donor properties as ammonia, and for the same reason; the molecule of ethylene diamine is therefore a donor at both ends and counts two towards the co-ordination-number of any metallic atom with which it may be combined.   Thus two optically active salts are known containing the complex cobaltic ion $[Co.2NH_3.(NO_2)_2.(NH_2.CH_2.CH_2.NH_2)]$·, and the structures assigned to them are A and B; they are mirror-images.   C, on the other hand, is an optically inactive isomer, and the difference between C and either A or B is similar to the difference between the isomeric platinic compounds just discussed.   Students of organic chemistry will understand why A and B are called the *cis*-isomers while C is a *trans*-isomer.   Werner also succeeded in preparing optically active salts containing no carbon atoms, thus disposing of the view that the presence of a carbon atom is necessary to optical activity.   The first compound of this type to be produced had the formula $[Co(Co.4NH_3.(OH)_2)_3]Br_6$.   The group $Co.4NH_3.(OH)_2$, like ethylene diamine, counts two towards the co-ordination-number of the central cobalt atom.

The Conception of Mesomerism.—If the formulae proposed

*M

on p. 340 and p. 337 for ozone and nitrate ion respectively, namely:
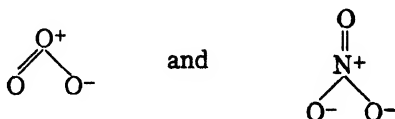
faithfully represented the structures of these molecules, we must find that the ozone molecule has the shape of a scalene triangle, and nitrate ion that of an isosceles triangle, for it is found that double bonds are invariably shorter than the corresponding single bonds. It is however known that both the O, O links in ozone are equal in length, as are all the N, O links in nitrate ion, the actual shapes thus being an isosceles and an equilateral triangle respectively.

In devising the original single formulae we have evidently arbitrarily selected certain oxygen atoms out of the total number in the molecule to participate in the double bonds. If such an arbitrary selection were not justified we must propose no less than three structures for nitrate ion, and two for ozone,
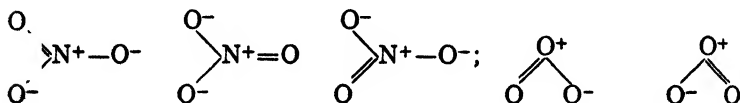
and it becomes clear that we have no ground for preferring one of these formulae above the others; we must in fact accept them as whole. To a chemist with a classical viewpoint this argument may well seem to be something like a verbal quibble, for it cannot be denied that the structures proposed for each molecular species are, in fact, *chemically* identical. The principles of quantum mechanics, however, demand that we regard the atoms of oxygen in each case as distinct entities, but deny that we can expect all the electrons in a given structure to be localized in particular chemical bonds. The quantum-mechanical view of ozone is that two of the total of six 'bonding' electrons serve to bind not two atoms but all *three* together, while in nitrate ion two out of the total of eight bonding electrons bind the three atoms of oxygen *equally* to the central nitrogen. To approximate to these representations of the two molecules, and still retain classical bond-diagrams, we must imagine our diagrams in each case taken in equal parts and 'fused' together, to give a *single* molecular structure. Equalization of the bond lengths, required to obtain agreement with experimental data, follows at once. Moreover, the originally localized negative charges

become equally shared by more than one oxygen atom in each molecule. It must be emphasized that such somewhat circuitous methods of arriving at a true representation of a molecule originate from our persistence in employing the traditional bond-diagrams. If ozone and nitrate ion are treated *ab initio* from a quantum-mechanical standpoint, without a classical chemical prejudgment, the totally symmetrical structures would emerge quite naturally and directly.

Although we have chosen to illustrate the phenomenon of meso-merism by two very simple molecules, the reader will at once realize what a widespread use must inevitably be made of the notion, so long as chemists wish to retain classical bond-diagrams. A further aspect of the matter is illustrated by the example of nitrosyl chloride. Classically we might be content with the diagram $O=N-Cl$, which at least assigns the correct valencies to all the atoms. However, it is found that the distance between the centres of the nitrogen and oxygen atoms is too short, and that between nitrogen and chlorine too long, to agree with this structure. Now we have reason to believe that the cation $(N\equiv O)^+$ is very stable (see p. 338), as is chloride ion Cl^-. The ionic, salt-like molecule, $(NO)^+.Cl^-$, might well be as stable as the covalent type previously written. It becomes apparent that we ought to accept both structures, but not in the crude form of a tautomeric mixture, for the (gaseous) compound certainly has no actual salt-like properties. Again there must be an imaginary process of ' fusing ' the two bond-diagrams. This case differs from those first noticed, for no chemist would accept the two diagrams as representing identical structures. Quantum-mechanical principles teach that mesomerism must be assumed (a) when the interatomic distances in the bond-diagrams are equal or at most slightly different, i.e. when the ' nuclear skeletons ' of the diagrams are nearly alike, (b) when in addition to the condition (a) the diagrams represent structures, which, if they separately existed, would have nearly equal stability, i.e. nearly equal energies of formation.

The term ' mesomerism,' by which we have described a matter of the most fundamental importance in chemistry, has unfortunately not gained the currency in chemical literature that it deserves. Most authors still appear to prefer the term ' resonance,' which, if employed (as it commonly is) away from its strictly quantum-mechanical context, is a wholly misleading description. It can hardly fail to give the impression that there is some actual vibra-tional relationship between the various bond-diagrams, concerned in the so-called ' resonance hybrid,' which is the result of what we have called ' fusion.' No such relationship exists. It must be clearly understood that the *real* phenomenon we are concerned with is

not at all the possibility of more than one bond-diagram (which is an accidental consequence of the way in which chemical thought has developed), but the participation of some at least of the bonding electrons in molecules in *all* the bonds of the molecule. A further consequence of mesomerism is that the stability of the single structure deduced as a true representation of a molecule is greater than that predictable for any of the fused structures: and the larger the number of structures that can legitimately written and then fused, the greater is the gain of stability. This important effect may be invoked to explain what had long puzzled chemists, why nitric oxide, NO, does not spontaneously polymerize to N_2O_2. The latter formula was to be expected on purely chemical grounds, for it would assign correct valencies to the two atoms. We may distribute the 11 available electrons in two ways, (a) and (b):

$$: \overset{\bullet}{N} \quad \vdots \quad \overset{\bullet\bullet}{O} : \qquad\qquad : \overset{\bullet\bullet}{N} \quad \vdots \quad \overset{\bullet}{O} :$$

(a)   (b)

and the fused form would be more stable than either (a) or (b). It is, in fact, so stable that the reaction

$$2NO \rightarrow N_2O_2$$
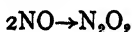
becomes endothermic.

It will be clear that the principle of mesomerism often relieves us of the old problem of decision between several classical formulae. We are not only allowed, but compelled, to accept all possible formulae that comply with the essential conditions mentioned above. In this connection we may refer again to carbon monoxide, to which, on semi-classical grounds, we assigned the single formula, $C^-\equiv O^+$ (p. 339). The principle of mesomerism directs us to give consideration also to alternative formulae, such as those represented by the electron assignments (c) and (d) below:

$$\overset{\bullet\bullet}{C} \quad \vdots \quad \overset{\bullet\bullet}{O} : \qquad\qquad : \overset{\bullet\bullet}{C} \quad \vdots \quad \overset{\bullet\bullet}{O}$$

(c)   (d)

Both of these formulae would be classically written as $C=O$. The true representation of carbon monoxide is a fusion of at least all these types, but at present we cannot decide with certainty what 'weight' in the 'fusion mixture' should be given to the individual (and hypothetical) structures. The classical bond-diagrams are proving too crude to represent the subtleties and complexities of chemical combination, especially as they necessarily imply that bonding electrons are *all* apportioned to linking only *pairs* of atoms.

PART III

THE ELEMENTS AND THEIR COMPOUNDS

CHAPTER XII

HYDROGEN

H $=$ 1·0080.   *Atomic Number,* 1

History.—The recognition of hydrogen as a distinct species of matter ('inflammable air') is due to CAVENDISH, who in 1766 obtained it by the solution of metals, e.g. zinc and iron, in dilute sulphuric and hydrochloric acids.   It was Cavendish also who showed it to be a constituent of water (1781-4), a fact in virtue of which LAVOISIER gave it the name *hydrogen,* or ' water-producer.'

Hydrogen is in many ways unique among the elements.   Not only is it the lightest of all substances, but it has the lowest atomic number and atomic weight of any element.   Its atom consists of a single proton accompanied by a single electron, and it is assigned to no group of the periodic table.   The hydrogen ion, which in the unsolvated form consists of a single proton, is one of the ions of water, is the essential constituent of aquo-acids, and plays a part of extreme importance in the chemistry of solutions.

Occurrence.—Hydrogen is one of the most abundant of elements, if the number of atoms is made the basis of the calculation, being preceded only by oxygen and perhaps by silicon, but its atomic weight is so small that on a weight basis it takes a much lower place in the list of relative abundance.   Nearly all the hydrogen in the world is in the form of water.   Some free hydrogen occurs in certain natural gases, and hydrogen is an essential constituent of living matter.   Little remains in the air, for the high molecular speed enables it to escape from the earth's gravitational field.

Preparation of Hydrogen.—Nearly all the commercial methods for preparing hydrogen start from water; some hydrogen, however, is isolated from coke-oven gases.

1. *Water-gas Process.*—The preparation of hydrogen from water-gas by the Bosch process is described in the section on synthetic ammonia (p. 388), and is carried out on an immense scale in most countries possessing a chemical industry.   Liquefaction technique has made such advances in recent years that in large installations of the future it may be decided to free the hydrogen from the accompanying gases by liquefying them.

2. *Coke-oven Gas.*—Coke-oven gas contains about 50 per cent of

hydrogen. The carbon dioxide and hydrogen sulphide can be removed chemically, and the gas is then compressed to ten atmospheres, a pressure at which the volatile hydrocarbons are liquefied. The liquid is a valuable source of ethylene. The uncondensed gas consists of hydrogen with a little carbon monoxide, from which it can, if necessary, be freed by passing it through liquid nitrogen.

3. *Liljenroth Process.*—In this process a mixture of phosphorus vapour and steam is passed over a catalyst:

$$2P + 8H_2O = 2H_3PO_4 + 5H_2.$$
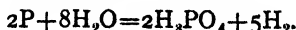
The phosphoric acid is combined with synthetic ammonia to make ammonia phosphate, used in fertilizers. This process was worked in Germany before the war of 1939–45.

4. *Electrolysis.*—The electrolysis of water, usually acidified with a little sulphuric acid, yields a very pure gas if the electrodes are separated by a diaphragm and care is taken to see that no mixing takes place. If the hydrogen is required under pressure, it is found to be more economical of power to generate it directly under pressure by electrolysis than to generate it under atmospheric pressure and to compress it afterwards. The electrolytic process is worked at several factories where ammonia is synthesized by the Claude process. Half the volume of oxygen is produced at the same time. Some of this can with advantage be used instead of air for the oxidation of ammonia to nitric acid, but oxygen is very largely a drug on the market and most of it is allowed to escape into the air.

Cheap electric power is essential to the process, but in the neighbourhood of abundant water-power it can compete successfully with the Bosch process. Immense quantities of hydrogen are produced during the manufacture of caustic soda by electrolysis. Some is used for the manufacture of hydrogen chloride, but most of it is run to waste, since the gas cannot be liquefied without great difficulty, and this makes economical transport impossible. In certain parts of Germany, however, a system of pipe-lines was developed in which hydrogen could be transmitted at high pressure from the centres of production to the factories where it was to be used.

5. *Reduction of Steam with Iron.*—When iron is heated in steam, triferric tetroxide and hydrogen are produced:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

The iron can then be regenerated by producer-gas or any other reducing gas. This process was formerly of importance, but is now used only in territories where fuel is scarce and power unusually expensive.

It will be seen that the manufacture of hydrogen has benefited

as much as any industry by modern applications of low-temperature and high-pressure technique. Besides the vast quantities used in the synthetic ammonia industry, production is absorbed in the manufacture of methyl alcohol and other synthetic organic chemicals (p. 571), in the hydrogenation of coal, and in the hardening of oils and fats (p. 802). Small quantities are used in the manufacture of hydrogen chloride, the oxy-hydrogen and atomic hydrogen blowpipes, and in filling balloons.

Laboratory Preparation.—In the laboratory hydrogen can be obtained from a cylinder or prepared by the action of dilute acids on metals. Zinc is the metal most commonly used for the purpose as, unless very pure, it dissolves readily in dilute sulphuric or hydrochloric acid. The action can be accelerated by the addition of a small quantity of a copper salt, which deposits copper on the zinc and forms a ' couple.' Kipp's apparatus or some similar device may be used. The gas is washed with water and dried with concentrated sulphuric acid, but it is not very pure, and cannot easily be freed from traces of air.

Fairly pure hydrogen can be obtained from zinc and sulphuric acid by washing the gas with alkaline permanganate solution, followed by caustic potash and drying agents. In this way oxides of sulphur, carbon, and nitrogen and hydrides of carbon, phosphorus, and arsenic can be removed, but a little air remains. The purest hydrogen is obtained by electrolysis. Carbonates are very undesirable impurities in the electrolyte, because carbon dioxide, which is soluble in water, might diffuse from the anode to the cathode and contaminate the hydrogen. A solution of baryta is therefore used, barium carbonate being insoluble in water. Back-diffusion of oxygen is minimized by the use of an apparatus of the familiar U-tube type, and if the apparatus is evacuated before electrolysis is begun, the only impurities in the hydrogen evolved are water-vapour and a little back-diffused oxygen. The latter is removed by passing the gas over asbestos on which palladium has been deposited (compare platinized asbestos). This leads to the formation of water, and the hydrogen is dried first with caustic potash and then with phosphorus pentoxide.

Hydrogen is also produced by the action of powerful reducing agents, such as the alkali-metals or chromous compounds, on water, or by the action of certain elements, such as zinc, aluminium, or silicon, on caustic alkalis, but these methods are not often employed.

Properties.—Hydrogen is a colourless gas with no taste or smell. It boils at $-253°$ and can be condensed to a colourless solid at $-259°$. Hydrogen is the lightest of known substances, having a density of only 8.985×10^{-5} gm. per c.c. at standard temperature and pressure. This corresponds with a diatomic molecule. At the boiling-point, the liquid has the very low density of 0.0711 gm.

per c.c. Hydrogen is only very slightly soluble in water (about 18 c.c. per litre at 12°), and forms no hydrates. On account of its low molecular weight, it diffuses very rapidly and can pass through such semi-porous materials as cork or rubber, a fact which it is often necessary to bear in mind in the laboratory. The large volumes of hydrogen which can be occluded by palladium are the subject of separate discussion (p. 811), but many other metals show this effect on a smaller scale, and at high temperatures many metals, iron among them, become permeable to the gas.

Allotropy of Hydrogen.—It can be shown by calculations based on wave-mechanics that hydrogen should be capable of existence in two allotropic forms, differing in nuclear spin. This view was confirmed in 1929, when by fractional adsorption on charcoal under pressure in liquid air, hydrogen was separated into its allotropes. These are called *ortho-* and *para*-hydrogen, and ordinary hydrogen is a mixture of the two in equilibrium, containing, at ordinary temperatures, just 75 per cent of the ortho-variety. There is a slight evolution of heat when the ortho- is converted to the para-variety, and the equilibrium proportion of the latter is consequently favoured by low temperatures. At liquid air temperatures the para-form predominates, and can be prepared nearly pure from ordinary hydrogen by adsorption at this temperature on charcoal, a method which avoids the extreme slowness with which equilibrium is reached in the gas phase. Even at room temperature para-hydrogen, prepared in this way, is stable for nearly a week when confined in glass vessels, though such catalysts as charcoal or platinum cause a very rapid reversion to the equilibrium mixture. At high temperatures the conversion takes place as a homogenous gas reaction of order 1·5. It is supposed that the para-hydrogen molecules are converted by collision with hydrogen atoms produced in the ordinary way by thermal dissociation:

$$H + H_2(para) \rightleftharpoons H + H_2(ortho).$$

The two forms of hydrogen show small but perceptible differences in physical properties. Ortho-hydrogen has not been obtained pure, as present methods allow the isolation only of the variety more stable at low temperatures, but the melting-point of para-hydrogen is 13·88° Abs., compared with 13·92° Abs. for the ordinary form, and there is also some difference in the boiling-point, since at 20·39° Abs., the boiling-point of ordinary hydrogen, the vapour pressure of para-hydrogen is 787 mm. The specific heats are also slightly different, and the conversion of one form to the other is usually followed by measuring the resistance of a hot wire in the gas (p. 99).

Active Hydrogen.—The dissociation of hydrogen into free atoms,

negligible at ordinary temperatures, occurs freely at very high temperatures, such as can be attained with the electric arc. The recombination of hydrogen atoms gives out much heat, $2H = H_2 + 103400$ cal. (cf. $2H_2 + O_2 = 2H_2O + 116000$ cal.), a fact used in the atomic hydrogen blowpipe. A stream of hydrogen is partially dissociated into atoms by passage through an arc struck between tungsten electrodes, and when directed on to the surface of a metal, the latter strongly catalyzes recombination, and may easily be fused by the heat liberated. Welding in a reducing atmosphere may thus be effected.

A more convenient method of producing atomic hydrogen is to submit hydrogen at normal temperature and low pressure to the action of high tension discharge in an appropriately constructed discharge-tube: one 2 cm. in diameter and about 2 metres long is suitable. The atomization is facilitated by the presence of water vapour (or oxygen). As might be expected, the atomic hydrogen so formed is a powerful reducing agent. The oxides and chlorides of copper, mercury, lead, and bismuth are reduced to metal rapidly at room temperature. Phosphorus pentoxide yields phosphine, and ethylene, ethane. The alkali-metals are converted into their hydrides in a strongly exothermic reaction, and hydrides are produced from elementary sulphur, phosphorus, arsenic, and antimony: even bismuth yields its hydride in traces.

As an example of the activity of ordinary hydrogen, it may be mentioned that when under pressure it will precipitate lead from lead nitrate solutions at 250° and upwards.

Hydrides.—At ordinary temperatures, however, hydrogen shows little chemical activity, and among the elements only fluorine, chlorine, and bromine will combine with it in the cold and in the absence of a catalyst, while with chlorine and bromine the action of light is necessary. The binary compounds of hydrogen are called *hydrides*, but the term is not usually applied to such compounds with non-metals as HCl, hydrogen chloride, or H_2S, hydrogen sulphide. The whole group of hydrides falls into three divisions which correspond at the same time with the properties of the compounds and with the position of the second element in the periodic table.

1. Elements on the right-hand side of the table, including all the non-metals (except the inert gases) as well as a few metals, form covalent hydrides. These are volatile colourless compounds, nearly all gaseous at room temperature. If we exclude the heavier hydrocarbons, the least volatile of them is probably water. The formula of these compounds is RH_{8-v}, where v is the group valency of the element R, but there are exceptions to this rule, such as the hydrides of boron or carbon, in which the molecule contains more

than one atom of R. In any group the stability of the hydrides decreases with increasing atomic number.

2. The alkali-metals and the alkaline-earth metals form electro-valent hydrides; these are colourless substances solid at room temperature. Their electrovalent character is attested by their low volatility, their behaviour on electrolysis, and their ionic crystal lattice. Thus lithium hydride has the sodium chloride crystal structure, and when fused and electrolysed gives hydrogen at the anode. The general formula is MH_v, where v is the group valency of the metal M.

3. Of the remaining elements many form no hydride, others form solid compounds of alloy type in which the valency relations, and even the composition itself, are sometimes not at all clear.

He

Li Be B C N O · F

Ne Na Mg Al Si P S Cl

A K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br

Kr Rb Sr Y Zr Nb Mo Ma Ru Rh Pd Ag Cd In Sn Sb Te I

X Cs Ba La & rare earths Ta W Re Os Ir Pt Au Hg Tl Pb Bi

Em EkaCs Ra Th U

CLASSIFICATION OF THE HYDRIDES

Preparation of the Hydrides.—The principal methods are as follows:

1. Direct combination. This seldom takes place unless a catalyst is present, but fluorine will combine with hydrogen even at very low temperatures. Heating is often sufficient—e.g. sulphur, iodine, or the alkali-metals—or the action of a catalyst under favourable conditions in the cold—e.g. oxygen or nitrogen. Certain elements, such as arsenic, will combine with 'nascent' hydrogen, that is, with hydrogen in the course of production in the same reaction mixture, and the unstable hydrides of tellurium or lead can be prepared by electrolysis of aqueous solutions with cathodes made from these metals. Other elements, such as carbon, will combine with hydrogen under the influence of the electric spark.

2. Many of the more volatile hydrides can be prepared by mutual replacement, e.g. hydrogen chloride from sodium chloride and sulphuric acid or phosphoric acid.

3. Certain hydrides, many of them difficult to prepare in other ways, can be obtained by the action of dilute acids on binary

compounds between the element concerned and magnesium, calcium, or aluminium. The hydrides of silicon, for example, are made from dilute hydrochloric acid and magnesium silicide.

The more important hydrides other than water are discussed in connection with the second element.

Hydrogen as a Reducing Agent.—At high temperatures hydrogen is a valuable reducing agent, but at ordinary temperatures its chemical inertness prevents much use being made of it. The displacement of hydrogen from solutions by the less electropositive metals is a reversible process, but it is usually very difficult to demonstrate the back-reaction, which in the absence of a catalyst takes place extremely slowly. Platinum is one of the best catalysts, and the hydrogen electrode, made of platinum covered with platinum black (p. 250), depends on the reversibility of the change: $H_2 \rightleftharpoons 2$ electrons$+2H^\cdot$. In the presence of platinum black gaseous hydrogen at normal pressure will reduce solutions of chlorates, cupric and silver salts. The reducing power of hydrogen appears to be greatly enhanced by the presence of metals. At ordinary temperature hydrogen released in acid solution by zinc or magnesium reduces arsenic compounds to arsine; nitrates are easily reduced to ammonia by hydrogen released in alkaline solution by aluminium, and electrolytic reduction at cathodes of mercury and lead is much used. At slightly higher temperatures in the presence, for example, of nickel, ethylene is reduced to ethane, and carbon monoxide to methane. The detailed mechanism is still somewhat controversial, but it is agreed that the effective reducing agency is the temporary binding of hydrogen atoms to the metal surface, and that metals show specific powers in so holding hydrogen.

Deuterium.—In 1919 STERN and VOLLMER searched for a heavy isotope of hydrogen by a diffusion process. They failed because they used hydrogen prepared by electrolysis, which, as is now known, contains very little of the heavy isotope. Indeed, until 1929 the existence of any such isotope seemed unlikely, since the atomic weight of hydrogen agreed closely with the mass of the proton determined with the mass-spectrograph. The discovery of the heavy isotopes of oxygen introduced a discrepancy into this agreement, and late in 1931 the existence of a hydrogen isotope of mass number 2 was announced in America by UREY, BRICKWEDDE, and MURPHY, who obtained it by the fractional evaporation of liquid hydrogen. They called it deuterium (symbol D). In the following year WASHBURN and UREY effected a partial separation of 'heavy water,' or deuterium oxide, D_2O, by electrolysing ordinary water, in which it occurs in very small proportion; the ordinary water is decomposed more rapidly than the heavy water.

Hydrogen is distinguished from all other elements by the ease

with which its isotopes can be separated, a consequence of the great relative difference in mass number. Ordinary hydrogen and ordinary water are believed to contain one atom of D in about 5,000 of H, and no segregation of isotopes has been detected in different natural waters. Fractional electrolysis of water is used as a method of concentration, and instead of ordinary water the electrolyte from commercial cells used in making oxygen and hydrogen may be used with advantage, as it already contains a concentration of D_2O above the normal. From 20 litres of such water (sp. gr. 1·000034) G. N. LEWIS and MACDONALD obtained as residue 0·12 c.c. containing over 99·99 per cent D_2O. This water has a sp. gr. of 1·1056. Mixed with ordinary water it may also be made by fractional distillation of water, preferably at reduced pressure, or by acting on dilute acids with iron or zinc, when the hydrogen in the residue retains an increased concentration of D. Thermal diffusion of hydrogen also leads, as would be expected, to separation of the isotopes, and so does fractional absorption. The atomic weights of the two isotopes, in terms of the O^{16} isotope, are 1·008123 and 2·01471.

Pure deuterium oxide freezes at $+3\cdot8°$ and boils at 101·42°. The vapour pressure is 87 per cent of that of ordinary water at 20° and 95 per cent at 100°; hence the advantage of distillation at low pressure when attempting the separation. Like ordinary water, heavy water has a temperature of maximum density, but it is 11·6° instead of 4°. This indicates a greater ' degree of association ' in heavy water, as also do the lower volatility, the higher heat of vaporization, and the much greater viscosity (28 per cent over that of ordinary water at 10°). The deuterium ion has a much reduced mobility, for which the increased viscosity of the medium is partly responsible. The solubility of many salts in heavy water is less than in ordinary water, though others are more soluble. The refractive index of heavy water is different from that of ordinary water, and this property, together with the density, is commonly used in determining the proportion of heavy hydrogen in a sample. Heavy water is very hygroscopic. It is believed not to support the life of higher organisms, for tobacco seeds die when placed in it, and the same has been said of tadpoles, worms, and fish.

Ammonia containing 99 per cent heavy hydrogen has been prepared from magnesium nitride and heavy water. Its freezing-point is 1·3° higher and its boiling-point 2·2° higher than that of ordinary ammonia, while the heat of vaporization is 193 calories per mole greater (compare heavy water). It smells like ordinary ammonia. Many organic compounds are known in which deuterium has been substituted for hydrogen. They do not differ markedly from the hydrogen compounds.

The Valency of Hydrogen.—A number of compounds is now known in which we are compelled, on experimental grounds, to assume that a pair of atoms from the group nitrogen, oxygen, and fluorine is brought, by the agency of hydrogen, into a close contiguity, or into a structural relationship, only comprehensible if in some way hydrogen exerts a bonding action between the pair of atoms. As examples may be quoted:

(1) The ion HF_2', which must be formulated $(F.H.F)^-$.

(2) Pairs of oxygen atoms in crystals of KH_2PO_4 and of $NaHCO_3$ are abnormally close together.

(3) The crystal structure of ammonium fluoride, NH_4F, in which nitrogen atoms are found with only four fluorine neighbours, instead of the eight to be expected if the structure were similar to that of other ammonium halides (p. 90).

(4) The constitution of ice and water, discussed on p. 103.

(5) The dimeric forms of the lower fatty acids, such as formic and acetic acids, have recently been proved (by the method of electron diffraction) to have the structure

$$R.C \overset{\displaystyle O - H \cdot \text{-} \text{-} \text{-} O}{\underset{\displaystyle O \text{-} \text{-} \text{-} \text{-} H - O}{\Big\langle \qquad \Big\rangle}} C.R$$
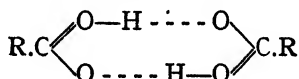
As explained on p. 347 hydrogen is debarred from exerting a normal bivalency, since in no case could the atom accommodate more than two electrons. The most probable explanation of the bonding effects exemplified above is one based on two unique properties of hydrogen: (*a*) The proton is unprotected by non-valency electrons, (*b*) the small radius of the (combined) hydrogen atom (approximately 0·3 Ångström units). Both these properties would enhance a purely electrostatic attraction between hydrogen and the atoms it links together. It is no doubt significant that the ' hydrogen bridge ' has only been observed between highly electronegative atoms. In the case of HF_2' it may well be assumed that the structure is purely ionic, and to be formulated as $F^-.H^+.F^-$. Such a view is strongly supported by the observation that in different hydrofluorides (e.g. of sodium, potassium, and ammonium) the distance between the fluorine atoms varies, and is thus affected by nature of the cation present. Such an effect would be expected if the binding in the anion were ionic. The best-known examples of hydrogen bridges between oxygen atoms may be regarded as originating either in the interaction of two hydroxyl groups (or ions) as in ice, or in the interaction of a hydroxyl group with doubly-bound oxygen, as in the fatty acids. It is almost certain that in

these examples the linking hydrogen atom remains closely asso-
ciated with the oxygen atom to which it would be solely attached
in the monomeric molecule, i.e. it does not assume a position equidis-
tant from each bound oxygen atom.   In such examples, therefore,
we must invoke dipole forces rather than simple ionic attractions.

WATER

Water, Hydrogen Oxide, Hydrogen Hydroxide, H_2O, is the most
abundant of all compounds, though the preparation of pure water
is a matter of great difficulty.   This arises from two causes: first,
that water dissolves traces of impurity from most of the materials
commonly employed for containing vessels; second, that water
contains dissolved gases very difficult to remove.   The first diffi-
culty can be overcome by the use of well-steamed-out vessels of
hard glass, or, better, of block tin or platinum or fused silica; but
the second is more serious.   For conductivity work the purest
water is required—the so-called ' conductivity-water '—and the
presence of carbon dioxide or ammonia, which commonly occur in
ordinary distilled water, is very undesirable, as solutions of these
gases are conductors of electricity.   A preliminary distillation
from sodium hydrogen sulphate, to retain ammonia, followed by
a second distillation from alkaline permanganate, to oxidize organic
impurities and retain carbon dioxide, gives fairly good water, but
a more laborious process is needed to secure the best results: this
usually consists of fractional condensation of steam or removal
of dissolved gases from water in a current of pure air, or a combina-
tion of both; see also p. 144.   During these operations the water
must be rigorously protected from the atmosphere.

Water is a liquid with a faint blue colour that is apparent
only when a considerable thickness is viewed.   It has no taste or
smell.   The freezing- and boiling-points of water under standard
pressure are taken as the fixed points of the Centigrade thermo-
metric scale, and are denoted by $0°$ and $100°$ respectively.   The
solid form, ice, has also a faint blue colour.   Since the density of
ice, 0·917 gm. per c.c. at $0°$, is much lower than that of water, the
freezing-point of water is lowered by the application of pressure,
but BRIDGMAN and others have found that at great pressures
several different forms of ice denser than water are produced.
There is no doubt that water, no less than ice, must be considered
as highly polymerized or macromolecular; this problem has been
discussed in connection with the association of liquids (p. 102).
The current explanation of the anomalous co-efficient of expansion
of water is given on p. 103.   The gaseous form of water, called

water-vapour or steam, is colourless. Its density at 100° and atmospheric pressure is rather higher than corresponds with the simple formula H_2O. If it be assumed that the polymerized molecules have the formula $(H_2O)_2$, then in steam at 100° these amount to about 9 per cent of the total number of molecules. The dissociation of steam into oxygen and hydrogen on heating is extremely slight, and amounts only to 4 per cent at 2500°; while at all temperatures up to 1000° or over it is imperceptible.

Water in the pure state is a very poor conductor of electricity, and is very weakly ionized. The ionic product [H'] [OH'], determined by the methods discussed in Chapter VI, p. 191, is only $1·1 \times 10^{-14}$ at 25°, and if any further dissociation of the hydroxyl ion takes place (OH'⇌H'+O'') it is too feeble to be detected. The chemical importance of water is due to its abundance and its solvent powers, which have made it the standard substance for our definitions of acidity and alkalinity, definitions which have had a great influence on chemical theory.

The oxidation of water produces oxygen (e.g. chlorine), or more rarely ozone (e.g. fluorine) or hydrogen peroxide (e.g. steam in the hydrogen flame). The reduction of water yields hydrogen. If we exclude the formation of additive compounds, the remaining reactions of water can be classified as *hydrolyses.* Certain aspects of hydrolysis have been discussed in Chapter VI, p. 203. The nature of the products depends chiefly on whether the water acts as a donor or an acceptor (p. 346), and the extent of the process depends on the tendency to ionization of the products and on their volatility. Thus, to compare a weak acid with a strong one, acetates are more subject to hydrolysis than chlorides, and to compare two strong acids, sulphates are less easily hydrolysed than chlorides.

Additive compounds between water and other substances, from which the water can easily be recovered unchanged, as for instance by reducing the pressure, are called *hydrates,* a name which should not be applied to the totally dissimilar class of substances the hydroxides. Hydrates are often formed by co-ordination of the water-molecule, which may act either as donor or acceptor, with other atoms or ions. It is very probable that the tendency of water to combine with solute ions is an important cause of the high ionizing power of water as a solvent.

The very important catalytic properties of water are discussed elsewhere (p. 215).

Natural Waters.—The most important natural waters are sea-water, rain-water, spring-water, and river-water. The total solid content of sea-water varies very much in different parts of the world. The Baltic Sea, which is fed by many rivers and where there is

little evaporation, contains some 0·5 per cent, the Atlantic about 3 per cent or 4 per cent, and the Dead Sea (really a lake) up to 25 per cent. The salts derived from ocean-water are largely sodium chloride, with smaller proportions of magnesium, calcium, and potassium salts, and of sulphates. Rain-water is the purest of natural waters, and besides dissolved oxygen, nitrogen, and carbon dioxide may contain only nitric acid or ammonium nitrate in small traces produced by fixation of atmospheric nitrogen in thunderstorms. In the neighbourhood of the sea rain-water usually contains salt, and in industrial areas much dust and some sulphuric acid from the combustion of coal. In spring-water, a large variety of substances may be found in different localities. Medicinal properties are often attributed to waters with a noticeable solute content. River-water is derived partly from rain and partly from springs, and is usually nearly pure unless contaminated by the discharge of sewage or factory waste.

For drinking-water the bacteriological analysis is at least as important as the salt content; but the presence of ammonia, whether free or combined, is always regarded with suspicion, for this substance is one of the products of the decomposition of animal matter.

Hardness of Water.—Spring-water usually contains in solution bicarbonates, chlorides, and sulphates of calcium and magnesium. These salts give the water properties, described as 'hardness,' which are inconvenient if the water is to be used for certain purposes. Hard water, for example, leaves a residue, or 'scale,' when evaporated in boilers, and when treated with soap precipitates a 'soap' of calcium or magnesium which is insoluble in water and therefore has no lathering properties. The hardness of water is usually measured by observing the volume of a standard soap solution needed to produce a permanent lather in it.

The bicarbonates are decomposed by boiling, which precipitates the

$$2HCO_3' = H_2O + CO_2 \uparrow + CO_3''$$
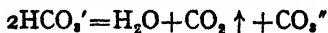
insoluble normal carbonates of calcium and magnesium, and leaves the water free from this cause of hardness, which is therefore described as 'temporary.' The same change can be brought about by making the solution alkaline with lime:

$$HCO_3' + OH' = CO_3'' + H_2O.$$
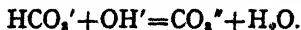
The 'permanent' hardness, due to chlorides and sulphates, can be removed by the addition of sodium carbonate, which precipitates the carbonates of calcium and magnesium, or by the use of a permutite filter (p. 540). Sodium salts in small concentration do not seriously affect the lathering power of soap.

OXYGEN

O=16·0000 [standard]. *Atomic Number*, 8

History.—The principal facts of the history of oxygen were discussed in the Historical Introduction (pp. 27–38).

Atomic Weight Standard.—The atomic number of oxygen is 8. Its atomic weight is taken to be exactly 16, and is used as the standard for the atomic weights of other elements. If the atomic weight of hydrogen, 1·0080, were taken as exactly 1, the atomic weight of oxygen would be 15·873. It has recently been discovered that oxygen contains very small quantities of isotopes of atomic weight 17 and 18. It will be noticed that if all the isotopes of oxygen had integral atomic weights on the basis of H=1, the atomic weight of oxygen would be slightly more than 16, instead of slightly less: the deviation of the atomic weight of hydrogen from unity when O=16 is to be explained, not by the existence of isotopes of oxygen, but by the theory of relativity (p. 327).

Occurrence.—Oxygen is the most abundant of all the elements, and is said to compose, by weight, about one-half of the crust of the earth, including the sea and the atmosphere. Water contains 89 per cent by weight of oxygen, and air 23 per cent. Together with carbon, hydrogen, and nitrogen, oxygen is an essential constituent of living matter.

Preparation.—Oxygen is prepared on a large scale by the fractional evaporation of liquid air, this process having taken the place of the old barium peroxide process. Immense quantities of oxygen are produced during the electrolysis of aqueous solutions, whether for the manufacture of hydrogen or for other purposes, but this oxygen is usually discharged into the air, as it is unprofitable to collect it unless some use can be found for it near at hand—as, for example, in the oxidation of ammonia to nitric acid. Most of the oxygen of commerce is used in oxy-hydrogen, oxy-coal gas, or oxy-acetylene blowpipes for cutting or welding metals, but small quantities are used in medicine.

In the laboratory oxygen is usually obtained from a cylinder of the compressed gas. Alternatively, it may be prepared by heating potassium chlorate, when the first action is the formation of potassium perchlorate, followed by the decomposition of this substance.

$$4KClO_3=3KClO_4+KCl. \quad KClO_4=KCl+2O_2 \uparrow.$$
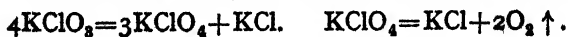
In the absence of a catalyst the action takes place at a fairly high temperature, and is then violent if not actually explosive; hence a catalyst is added, usually manganese dioxide. If this substance is used it is wise to make sure that it has not been adulterated with

charcoal, which causes dangerous explosions. Sodium chloride is sometimes added to the reaction mixture. The principal impurities in oxygen prepared by this method are *nitrogen* and *argon*, which must be driven from the apparatus before the collection of gas is begun, and *chlorine*, which can be absorbed in caustic alkali solution. Oxygen can be dried with any of the usual drying agents.

Oxygen can also be obtained by heating potassium permanganate, mercuric oxide, and other substances, or by the decomposition of hydrogen peroxide or aqueous solutions of sodium peroxide. The purest gas is obtained by electrolysis of a solution of a chromate or a permanganate in dilute sulphuric acid. If dissolved gases have been removed from the acid solution by boiling it before adding the oxidizing agent, water is the only detectable impurity in the gas rising from the anode.

Properties.—Oxygen is a colourless gas, without taste or smell, which at $-183°$ can be condensed to a pale blue liquid, freezing at $-219°$. Liquid oxygen is attracted by a magnet. Solid oxygen exists in at least two crystalline forms, the reason for the dimorphism remaining obscure. The vapour density of oxygen shows the molecule to be diatomic. The gas is only slightly soluble in water (less than 40 c.c. per litre of water at $12°$), but is considerably more soluble in alcohol.

At ordinary temperatures oxygen reacts with the majority of substances either slowly or not at all, but nearly all the elements will combine directly with oxygen if heated to a sufficiently high temperature in the gas. Gold, platinum, and the halogens cannot be made to combine directly with oxygen. Binary compounds of oxygen are called *oxides*, and oxides have been prepared of all the known elements with the exception of the inert gases. The oxides are compounds which may be solid, liquid, or gaseous, soluble in water or nearly insoluble, and in fact they display an extreme variety of properties. The most useful classification depends chiefly on the behaviour with acids and bases.

(i) *Acidic oxides* react with bases to form salts with the element of the oxide in the anion, e.g. phosphoric oxide, sulphur dioxide, silica.

(ii) *Basic oxides* react with acids to form salts with the element of the oxide in the cation, e.g. calcium oxide, ferrous oxide, lead monoxide.

(iii) *Amphoteric oxides* show both acidic and basic properties. Since nearly all oxides are in some degree amphoteric, the term is usually restricted to those in which the acidic and basic properties are of comparable strength, e.g. aluminium oxide, antimony trioxide.

(iv) *Peroxides* contain the grouping —O—O—, and yield hydrogen peroxide with dilute acid. Examples are sodium peroxide and barium peroxide.

The nature of the oxides formed by the elements varies in a fairly regular way with the position of the elements in the periodic table. Those metallic elements lying on the left of the table (in the form on p. 303) form chiefly basic oxides and peroxides, while the elements on the right are non-metals and form acidic oxides. When an element forms more than one oxide, the acidity increases with the valency: manganese and chromium offer good examples of this phenomenon. In each group of the table the acidity of the highest oxides decreases with increasing atomic number, and in passing from left to right along a horizontal series the acidity of the highest oxides increases, as has already been pointed out.

The affinity of the oxides for water is extremely variable. Some combine with it with avidity to form compounds called *hydroxides*, which contain the univalent hydroxyl group, OH. The term ' hydroxide ' is, however, usually restricted to the hydroxides of the metals, which, if soluble in water, are called *alkalis*. Water itself remains outside any classification of the oxides based on alkalinity or acidity, since these terms are defined with respect to the constituent ions of water, but alternative definitions are possible and have on occasion been used (see, for example, p. 192).

Mixtures of oxygen with hydrogen and other inflammable gases are explosive unless either constituent is present in very large excess. The combustion of hydrogen, acetylene, or coal-gas in oxygen produces an intensely hot flame used in the blowpipe. In this instrument the hydrogen and oxygen are fed from separate cylinders into concentric tubes and meet at the nozzle. The combination of oxygen with hydrogen is one of the numerous gas reactions which at ordinary temperatures have a great affinity but a negligible velocity. At room temperature no trace of reaction can be observed, but an explosion takes place if any part of the mixture is heated to 800°—say with a match or by a spark—or exposed to a fragment of platinum black or any other suitable catalyst. The perfectly dry gases will combine if a powerful firing spark is used.

Oxidation and Reduction.—The addition of oxygen to a substance, the removal of hydrogen from it, or any similar alteration of its electropositive or electronegative constituents, is called *oxidation*. The reverse process is called *reduction*. When one substance is oxidized another must be reduced, though in an electrolytic cell oxidation may take place at one electrode (the anode) and reduction at the other (the cathode).

Oxidation of an ion or molecule may also consist in the removal of electrons from it. Some examples of both types may be given.

Transfer of Oxygen Atoms.—Ferric oxide oxidizes aluminium to aluminium oxide, and is itself reduced to iron:

$$Fe_2O_3 + 2Al = 2Fe + Al_2O_3.$$
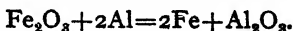
Hypochlorites oxidize bromides to bromates:

$$3ClO' + Br' = 3Cl' + BrO_3'.$$
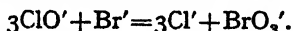
Transfer of Hydrogen Atoms.—Hydrogen bromide is oxidized to bromine by chlorine, which is reduced to hydrogen chloride:

$$2HBr + Cl_2 = Br_2 + 2HCl.$$
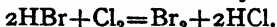
Transfer of Electrons.—Ferric salts oxidize iodides to iodine, and are reduced to ferrous salts:

$$2Fe''' + 2I' = 2Fe'' + I_2.$$
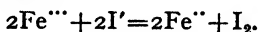
Electrolytic Oxidation.—Chlorides can be oxidized at an anode to chlorine, and sulphates to persulphates. Compensating reductions must take place at the cathode:

$$2Cl' - 2 \text{ electrons} = Cl_2.$$
$$2SO_4'' - 2 \text{ electrons} = S_2O_8''.$$

Oxidation in Acid Solutions.—In many oxidations in aqueous solution oxygen atoms are reduced to hydroxyl ions:

$$O_2 + 4 \text{ electrons} = 2O''. \qquad 2O'' + 2H_2O = 4OH'.$$

Such processes usually require the presence of an acid. Thus solutions of iodides are oxidized by hydrogen peroxide in the presence of an acid, but not in neutral solution:

$$H_2O_2 + 2I' + 2H' = 2H_2O + I_2.$$

Atomic Oxygen.—By passing oxygen at low pressure (1 mm.) through a silent electric discharge, many of the molecules are split up into single atoms; and although these quickly recombine to form the ordinary diatomic molecules, some of the properties of atomic oxygen have been studied. It will, for instance, decompose hydrocarbons, the reactions being accompanied by an intense blue chemiluminescence; and will melt platinum owing to the great heat evolved when the atoms recombine—a reaction greatly catalysed on the surface of the metal. It will also oxidize bromine to BrO_2, and hydrogen bromide to bromine and water.

Ozone, O_3

History.—The peculiar smell caused by the passage of an electric discharge through air seems to have been first observed by VAN MARUM in 1785. SCHÖNBEIN (1839-40) showed that the smell was due to a new gas, which he called ' ozone,' from the Greek

ὄζειν, to smell. The constitution of the gas, O_3, was established by SORET (1866).

Preparation.—The formation of ozone from oxygen according to the equation $3O_2 \rightleftharpoons 2O_3$ is a strongly endothermic reaction, and the equilibrium yield is consequently promoted by high temperature, as well as by increased pressure. At room temperature and atmospheric pressure the equilibrium yield of ozone is practically nil, and even at 2000° it is only 1·5 per cent. The formation of ozone by simply heating oxygen can, however, be demonstrated by plunging a white-hot platinum wire into liquid oxygen. The oxygen in contact with the wire is quickly heated and as quickly cooled, and there is no time for the ozone produced at the high temperature to decompose before it reaches a low temperature at which the rate of decomposition is very slow.

A more practicable method for the preparation of ozone is the action of the silent electrical discharge on oxygen at room temperature. A simple form of apparatus for this purpose is shown in the diagram (Brodie's ozonizer). A double tube is immersed in dilute sulphuric acid, with which the inner tube is also filled, and the discharge from an induction coil is passed across the annular space
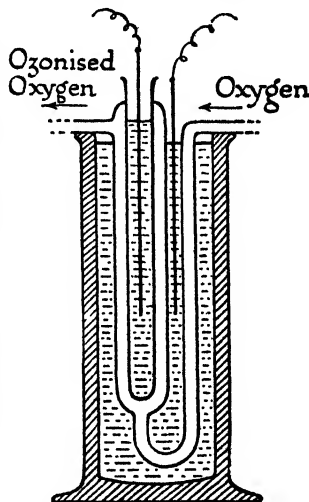
FIG. 102. BRODIE'S OZONIZER

while oxygen is allowed to flow through it. Other electrolytes will do as well. If air is used instead of oxygen some oxides of nitrogen may be formed at the same time, particularly if sparks are allowed to pass. In commercial plants it is important that this should be avoided, and the discharge is usually passed between glass plates covered with wire gauze, while a slow current of air passes through the system.

Ozone is also produced from air or oxygen under the influence of ultra-violet light, and is formed, together with oxygen, at the anode during the electrolysis of aqueous solutions with a high current density. Anodes, such as those of smooth platinum, which have a high oxygen over-voltage, are the best. The action of fluorine on water produces oxygen mixed with a considerable proportion of ozone.

Since ozone is unstable at ordinary temperatures it is essential,

N

during its preparation, to keep the apparatus cool, to diminish as far as possible the rate of decomposition. Pure ozone free from oxygen is difficult to prepare, but a product containing 80 per cent or 90 per cent of ozone can be obtained by cooling in liquid air the gas issuing from an efficient ozonizer. Since ozone is less volatile than oxygen, the residue which remains after most of the condensed gas has evaporated is very rich in ozone. A purer product can be obtained by liquefaction of ozonized oxygen, followed by fractional distillation of the liquid. The ozone so prepared melts at $-250°$ and boils at $-112°$. It decomposes fairly rapidly in the gaseous state even at low temperatures, but it has been found possible to measure its vapour density, which corresponds with the formula O_3.

Properties.—Ozone in the gaseous state has a very pale blue colour, and when condensed to a liquid is much darker in colour than liquid oxygen. Liquid ozone is dangerously explosive. Ozone has a very powerful smell not unlike that of chlorine, and is poisonous, but in very low concentrations it is perhaps beneficial, since it destroys bacteria present in the air. Indeed, slightly ozonized air is much used in ventilation, as for instance on the tube railways in London, where the smell of the gas is often noticeable. In the neighbourhood of electrical machinery, too, the smell of ozone can often be detected, but the odour sometimes attributed to ozone at various seaside resorts is mainly due to decaying seaweed.

The composition of ozone remained undetermined by the earlier investigators, on account of the difficulty of preparing the pure gas; it was first established by SORET in 1866. It could be shown without difficulty that ozone was an allotropic form of oxygen with a different molecular weight. Soret took two equal volumes of the same specimen of ozonized oxygen, and converted one to oxygen by heating it, noting the increase in volume after the sample had been restored to its original temperature and pressure. The ozone in the second sample was absorbed in cinnamon oil, in which it is very much more soluble than is oxygen, and the contraction was noted. From this second experiment the volume of the ozone present in the ozonized oxygen, under the given conditions of temperature and pressure, could be directly measured, and was found to be twice the expansion produced by conversion to oxygen. It follows that ozone increases in volume by one-half when converted to oxygen, so that ozone must have the formula O_3, the decomposition being represented: $2O_3 \rightarrow 3O_2$. For the structure of ozone see p. 352.

Ozone is only very slightly soluble in water, which is chemically unaffected by it, but it dissolves freely in the essential oils such as oil of cinnamon or turpentine. The power which these solvents possess of dissolving the gas is connected with the presence of a

double bond in their molecular structure. Ozone combines with nearly all, perhaps with all, unsaturated carbon compounds, e.g. ethylene, to produce unstable additive compounds called *ozonides*, which are of some importance in organic chemistry, particularly in investigations of structure. For this reason ozone rapidly corrodes rubber, and also attacks cork, though more slowly. The spontaneous decomposition of ozone takes place slowly at ordinary temperatures and more rapidly on warming: it is also greatly accelerated by certain catalysts, such as carbon or cupric oxide.

$$CH_2 \quad \overset{\displaystyle O}{\underset{\displaystyle O-O}{\diagup}} \quad CH_2$$

ETHYLENE OZONIDE
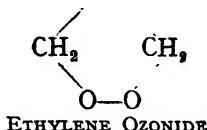
Ozone is a powerful oxidizing agent which under suitable conditions will convert all metals except gold and some of the platinum group to their oxides; in these changes it usually behaves like a specially active form of oxygen. Mercury exposed to ozone, even in small concentration, is superficially attacked and tends to stick to the glass vessel in which it is confined: this 'tailing' is one of the tests for ozone. The oxidation of manganous solutions by ozone may lead to a variety of products and is discussed elsewhere (p. 764). Iodides are oxidized to iodine even in neutral solution:

$$2I' + O_3 + H_2O = 2OH' + I_2 + O_2.$$
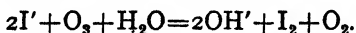
Oxygen is set free at the same time, so that only one of the three oxygen atoms of the ozone molecule is effective in this reaction, but in acid solution hydrogen peroxide is also produced, while in alkaline solutions some at least of the ozone forms an iodate according to the equation $I' + O_3 = IO_3'$. Ferrous solutions are oxidized to the ferric state, ferrocyanides to ferricyanides, nitric oxide to higher oxides, hydrogen sulphide to sulphur, and sulphur in suitable conditions to sulphur dioxide, or, in the presence of moisture, to sulphuric acid. Halogen is set free from all the hydrogen halides except hydrogen fluoride, e.g.:

$$2HBr + O_3 = Br_2 + O_2 + H_2O.$$

Methane is oxidized in the cold to carbon dioxide and water, but hydrogen and nitrogen are unaffected under ordinary conditions.

Ozone can be detected by its oxidizing properties, but it is more difficult to distinguish it from other oxidizing agents, and particularly from hydrogen peroxide. However, ozone is unique in giving a violet colour with test-papers soaked in solutions of an

organic compound usually called ' tetramethyl base,' [1] and, unlike hydrogen peroxide, it is unaffected by a solution of potassium permanganate.

Ozone is used in artificial ventilation, in purifying water from organisms, and in bleaching.

In the lower atmosphere, ozone sometimes occurs in traces (e.g. one part in 10,000,000). In the higher atmosphere, at a distance of some forty to fifty kilometres from the ground, it is present in large quantities, the amount varying with the latitude and with climatic conditions.

Hydrogen Peroxide, H_2O_2

History.—Hydrogen peroxide was discovered by THENARD (1819), though it was not prepared pure until 1894, by WOLFFENSTEIN.

Preparation.—The formation of hydrogen peroxide from oxygen and water, $2H_2O+O_2=2H_2O_2$, resembles the conversion of oxygen to ozone in that it is an endothermic reaction which gives an appreciable equilibrium yield of the product only at very high temperatures. Even at 2000° the yield of hydrogen peroxide is minute, but traces are formed when steam is blown through a flame of burning hydrogen, or when such a flame is directed on to ice. The thermal equilibrium can, however, be displaced by electrical methods (*compare* ozone). At the temperature of liquid air the brush discharge produces a good yield of hydrogen peroxide from oxygen mixed with either so little or so much hydrogen that the mixture is not explosive, and at ordinary temperatures hydrogen peroxide sometimes appears at the anode during the electrolysis of acid solutions.

None of these methods is put to practical use. On a commercial scale hydrogen peroxide is prepared from permonosulphuric acid by adding sulphuric acid and distilling at low pressure:

$$SO_5''+H_2O=SO_4''+H_2O_2\uparrow,$$

or from barium peroxide and dilute sulphuric acid. In the laboratory hydrogen peroxide is best prepared by distilling at low pressure and a temperature of 50°–60° dilute sulphuric acid which has been nearly neutralized by sodium peroxide:

$$Na_2O_2+2H\cdot=2Na\cdot+H_2O_2\uparrow.$$
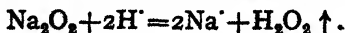
The mixing is carried out in a freezing-mixture, with constant stirring, and the solution can be concentrated before distillation by allowing the sodium sulphate decahydrate, $Na_2SO_4.10H_2O$, to

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[1] Tetramethyl—*p*—*p'*—diaminodiphenylmethane.

settle out, carrying with it a good deal of the water. Commercial sodium peroxide always contains a little chloride, and hydrogen chloride therefore finds its way into the distillate, from which it must be removed, if a very pure solution is required, by a further low-pressure distillation from silver carbonate. This method has superseded the former preparation of hydrogen peroxide from barium peroxide and sulphuric acid.

In another method, carefully purified barium peroxide (p. 493) suspended in water is treated with phosphoric acid, when barium phosphate is precipitated and an aqueous solution of hydrogen peroxide is formed:

$$3BaO_2 + 2H_3PO_4 = Ba_3(PO_4)_2 \downarrow + 3H_2O_2.$$
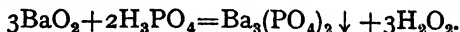
The phosphoric acid is recovered by the action of sulphuric acid upon the barium phosphate:

$$Ba_3(PO_4)_2 + 3H_2SO_4 = 3BaSO_4 \downarrow + 2H_3PO_4,$$
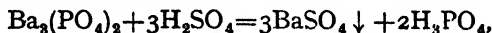
and the barium sulphate formed as a by-product is sold as a pigment ('blanc fixe'). The solution of hydrogen peroxide obtained in this way is very pure and usually contains about 45 gm. of H_2O_2 per litre.

The volatility of hydrogen peroxide is comparable with that of water, and hence solutions of the peroxide in water cannot be concentrated by evaporation beyond a certain point, apart from the losses caused by decomposition. By evaporation *in vacuo* hydrogen peroxide solutions can be concentrated to about 70 per cent, though not without the risk of explosion. A better method is to mix the solution with an inert hydrocarbon such as cymene and distil at low pressure, when nearly all the water collects with the cymene in the distillate: a process somewhat similar to steam distillation. Nearly pure peroxide can be prepared by freezing concentrated solutions and removing the water as ice.

Properties.—Hydrogen peroxide is nearly colourless, but its pale blue colour is probably intenser than that of water, though not at all noticeable under ordinary conditions. At ordinary temperatures it is a viscous liquid with a density of about 1·44. This liquid freezes at −1°, and under 20 mm. pressure boils in the neighbourhood of 60°. The structure of hydrogen peroxide is probably HO.OH, the two hydrogen atoms being arranged in directions perpendicular to one another and to the axis joining the oxygen atoms. Hydrogen peroxide mixes with water in all proportions, and is also very soluble in certain organic liquids, e.g. alcohols and ethers. With such solvents and water it gives a nearly constant distribution ratio, indicating a similarity of molecular species in the two liquids. Cryoscopic measurements show

that in water the hydrogen peroxide molecule is single, and the same is true of the vapour (but see p. 104). A smaller degree of association is probably the reason for the volatility of hydrogen peroxide as compared with water. The peroxide is also very soluble in such basic solvents as aniline or quinoline, with which it combines; the distribution ratio between quinoline and water actually favours the quinoline.

Hydrogen peroxide is an exceedingly weak acid with a dissociation-constant of about $2 \cdot 5 \times 10^{-12}$ at $25°$—this applies to the first dissociation, $H_2O_2 \rightleftharpoons H^{\cdot} + HO_2'$, the second dissociation being imperceptible. So weak an acid is it that solutions of the peroxides of the alkali-metals and alkaline earths, such as Na_2O_2, which are best regarded as salts of hydrogen peroxide, are almost wholly hydrolysed, only a small proportion of the ion HO_2' remaining unconverted to hydrogen peroxide, while there is nothing to show that the ion O_2'' is present at all. Solutions of hydrogen peroxide slowly decompose into water and oxygen, and this decomposition is greatly accelerated if the solution is made alkaline or is warmed. It was formerly supposed that this was a homogeneous reaction, but it has been shown that if extraordinary precautions are taken to free the system from dust and other impurities, concentrated solutions of hydrogen peroxide can be preserved unchanged in silica vessels for days even at $60°$. The decomposition is in fact a heterogeneous reaction which takes place on the surface of dust particles or of the containing vessel. It has long been known that the slow decomposition of ordinary hydrogen peroxide solutions can be retarded, though never altogether arrested, by the addition of certain anticatalysts or inhibitors. Organic substances such as ether, glycerol, acetanilide, or barbituric acid are most commonly used, but most acids, including dilute sulphuric acid, are quite effective. The action of these substances is due to their power of ' poisoning ' the dust particles which cause the decomposition of the hydrogen peroxide, and the special efficacy of acids is easily understood when we remember that the most active particles must be those which readily adsorb the weak acid hydrogen peroxide and will therefore readily adsorb other acids as well. Since the complete removal of dust has not yet been found practicable on a commercial scale, nearly all commercial samples of hydrogen peroxide, including some of those sold as specially pure, contain a preservative, which must be removed by distilling off the peroxide at low pressure if a pure solution is wanted. Hydrogen peroxide solutions should be kept in the dark in stoppered bottles.

Many catalysts for the decomposition are known, among the best being manganese dioxide and platinum black or colloidal

platinum. Copper salts have a very pronounced catalytic effect upon the decomposition of hydrogen peroxide solutions. A solution containing 30 gm. H_2O_2 per litre and 10 parts per million of copper was found to lose 57·4 per cent of its peroxide after refluxing for 1 hour, and 96·3 per cent after 2 hours. Hydrogen peroxide solutions are also rapidly decomposed by neutral iodide solutions, from which, however, they liberate no measurable quantity of iodine (*contrast* ozone), the action being purely catalytic. The concentration of hydrogen peroxide solutions is sometimes roughly expressed by the volume of oxygen which can be obtained by their decomposition into oxygen and water; thus the ' 20-volume ' solution, a form in which the peroxide is often sold, evolves twenty times its own volume of available oxygen. A convenient source of hydrogen peroxide is the crystalline compound $CO(NH_2)_2.H_2O_2$, which it forms with the weak base urea.

Hydrogen peroxide is a powerful oxidizing agent used for bleaching delicate fabrics and as a disinfectant. Its advantages for these purposes lie in the perfectly harmless character of the products of decomposition, oxygen, and water. Concentrated solutions will, however, blister the skin.

Hydrogen peroxide may be regarded as a compound formed by the oxidation of water: $H_2O+O=H_2O_2$, or by the reduction of oxygen: $O_2+2H=H_2O_2$. It can act as an oxidizing agent or as a reducing agent, producing water and oxygen respectively. The equations are $H_2O_2=H_2O+O$ and $H_2O_2=O_2\uparrow+2H$, but they may be written ionically: $H_2O_2+2H^{\cdot}=2H_2O-2$ electrons, and $H_2O_2+2OH'=2H_2O+O_2\uparrow+2$ electrons. An oxidizing agent, from the ionic standpoint, is a substance that absorbs electrons, a reducing agent one that supplies them. From the ionic equations we should expect the oxidizing powers of hydrogen peroxide to be promoted by acidity, and this can be verified by experiment. In alkaline solution ferricyanides are reduced to ferrocyanides, while in acid solution the reverse change takes place:

$$2Fe(CN)_6'''+H_2O_2+2OH'=2Fe(CN)_6''''+2H_2O+O_2\uparrow$$
$$2Fe(CN)_6''''+H_2O_2+2H^{\cdot}=2Fe(CN)_6'''+2H_2O.$$
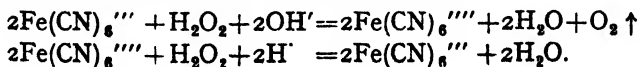
Silver oxide is reduced to silver:

$$Ag_2O+H_2O_2=2Ag+H_2O+O_2\uparrow.$$

The powerful oxidizing agent potassium permanganate oxidizes hydrogen peroxide even in acid solution:

$$2MnO_4'+6H^{\cdot}+5H_2O_2=2Mn^{\cdot\cdot}+5O_2\uparrow+8H_2O.$$
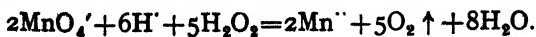
This reaction is used in the estimation of hydrogen peroxide by volumetric analysis. In the presence of organic preservatives

which might reduce the permanganate, the oxidation of an acid iodide solution is more suitable:

$$H_2O_2 + 2I' + 2H^{\cdot} = I_2 + 2H_2O.$$
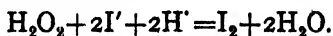
The reaction takes place rather slowly, and hydrogen peroxide is catalytically decomposed by iodide ions, so it is best to catalyse the oxidation of the iodide with a little ammonium molybdate. The iodine set free is titrated with thiosulphate.

Hydrogen peroxide produces peroxy-compounds with the oxy-salts of the elements of the A subgroups of Groups IV and VI. Thus with chromates a blue solution of an oxide CrO_5, which can be extracted with ether,[1] is obtained, and with titanic salts an orange solution. These reactions can be used as tests for all the substances concerned. With other salts, such as sodium phosphate, hydrogen peroxide combines to form compounds that appear to contain hydrogen peroxide of crystallization, since the peroxide can be wholly removed by shaking with ether. From alkaline solutions of the salts of the alkaline-earth metals, hydrogen peroxide precipitates peroxides such as $CaO_2.8H_2O$.

If hydrogen peroxide is added to an alkaline solution of pyrogallol and formaldehyde (H.CHO) it is reduced to gaseous hydrogen, the formaldehyde being oxidized to formic acid:

$$2H.CHO + H_2O_2 = 2H.COOH + H_2 \uparrow.$$
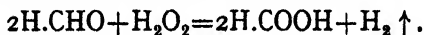
This reaction is of interest since during its progress light is emitted (*chemiluminescence*), as may be seen if the experiment is carried out in a darkened room.

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[1] And pours a deeper blue to Aether's bound.
                                    WORDSWORTH, *An Evening Walk.*

CHAPTER XIII

$N = 14 \cdot 008.$ *Atomic Number, 7*

General.—Nitrogen is the lightest member of Group V, and its atom has five valency electrons. In its binary compounds its valency is, however, unlike that of phosphorus, confined to three, in accordance with the covalency maximum rule, which rigidly limits the covalency of elements in the first short period to four. Consequently the tervalent compounds of nitrogen contain a lone pair of electrons, which gives them the donor properties so conspicuous in ammonia, the most important compound of this type. When this lone pair of electrons is satisfied by co-ordination with an acceptor, nitrogen has reached its permissible maximum covalency of four. To this circumstance are due not only the series of ammonium salts, but also the often very stable additive compounds which ammonia forms with so many salts. In this respect ammonia resembles water, and a comparison has often been drawn between ammonium salts and acids dissociated in water:

$$H_2O + HX \rightarrow H.H_2O^{\cdot} + X'.$$
$$H_3N + HX \rightarrow H.H_3N^{\cdot} + X'.$$
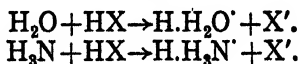
Nitrogen differs from the later members of the group by its abundance, its occurrence in the atmosphere, its much greater volatility, the great stability of its diatomic molecule, the relative unimportance of its only known allotrope, and its chemical inertness. Its hydride is far more basic than other Group V hydrides. It occupies a position near the centre of the first short period, and like the neighbouring element carbon forms very stable compounds with both oxygen and hydrogen. It also resembles its neighbours carbon and oxygen in its curious reluctance to combine directly with the halogens.

The atom of nitrogen was decomposed by RUTHERFORD in 1919 by the method of α-ray bombardment.

The Circulation of Nitrogen in Nature.—Together with carbon, hydrogen, and oxygen, nitrogen is an essential constituent of living matter. Since this is subject to death and decay, and is also constantly changing through assimilation and excretion, part of the world's nitrogen is in continual change, but this is only a small part of the total nitrogen present in the world. The principal

*N

possibilities are shown in the diagram, which represents a scheme sometimes referred to as the 'nitrogen cycle.' Only exceptional plants are able to derive their nitrogen direct from the air—a transformation which they accomplish with the help of 'symbiotic' bacteria attached to their roots—and most can assimilate it only when it is presented in the form of a compound soluble in water,
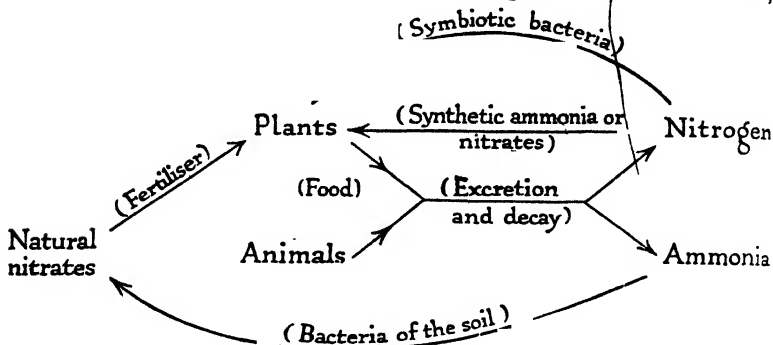
FIG. 103. THE NITROGEN CYCLE

usually a nitrate or an ammonium salt. The nitrogen returned to the soil by the death and decay of animals and plants, or by the excretion of the former, is liberated partly as atmospheric nitrogen, the greater part of the residue appearing as ammonia, which by the action of bacteria present in soil is oxidized to a nitrate. Since cultivation soon exhausts the natural nitrates present in soil, these must be supplemented by fertilizers or manure. The principal nitrogenous fertilizers are dung, the nitrate deposits of South America, and synthetic ammonium compounds or nitrates made from atmospheric nitrogen.

AIR

The proportions of oxygen and nitrogen will differ according as they are stated by weight or by volume, and are in any event not absolutely constant in different parts of the earth or even at different times. As will be shown in the next chapter, air contains not only these two gases but also five others—the inert gases of the atmosphere—in addition to a little carbon dioxide and various impurities in the neighbourhood of towns, houses, or animal or vegetable matter. Air also contains water-vapour and dust, a name which may be taken to include all floating solid impurities. Representative values for the proportions by volume of the gases present in pure dry air are: nitrogen 78·0 per cent, oxygen 21·0 per

cent, inert gases 0·9 per cent, carbon dioxide 0·03–0·04 per cent. If the calculation is made by weight, the proportions of nitrogen and oxygen come to about 75·5 per cent and 23·2 per cent. At considerable heights above the surface of the earth, the proportion of the heavier constituent, oxygen, decreases, and that of the lighter constituent, nitrogen, increases; and at great heights—a hundred kilometres or more—there may be larger proportions of the light rare gas helium. Near the surface of the earth the proportion of helium is exceedingly small.

NITROGEN

Preparation.—Nitrogen may be isolated from the air by removing carbon dioxide and oxygen from it by combination with suitable reagents, but the product is contaminated with the inert gases of the atmosphere. Since these gases have no chemical properties their presence is for many purposes no disadvantage. Hot copper
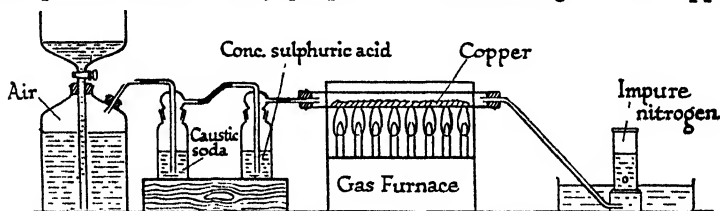
FIG. 104. THE PREPARATION OF NITROGEN FROM AIR

is commonly used for removing the oxygen, with which it forms cupric oxide: a suitable apparatus is shown in the diagram. The apparatus must be run for some time before any gas is collected, and the product, if collected over water, will inevitably contain a small proportion of oxygen, since oxygen is slightly soluble in water.

Nitrogen is generally obtained in the laboratory by heating (in solution) ammonium nitrite, for which a mixture of sodium nitrite and an ammonium salt may be substituted:

$$NH_4NO_2 = N_2 \uparrow + 2H_2O \uparrow.$$
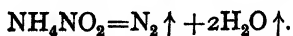
The gas usually contains a little nitric oxide as impurity, which can be oxidized to nitric acid, and retained, by an acid dichromate solution. Nitrogen can be dried by any of the usual agents. For the preparation of the pure gas, the interaction of hot nitric oxide and ammonia on a copper catalyst has been recommended:

$$6NO + 4NH_3 = 5N_2 + 6H_2O.$$
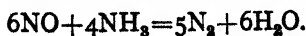
Excess of ammonia is removed by concentrated sulphuric acid. Nitrogen, containing only traces of oxygen, can also be obtained from a cylinder of the compressed gas, made by the liquid air process.

The two most important sources of industrial nitrogen are liquid air and producer-gas (p. 569). Since the boiling-point of nitrogen is —195°, while that of oxygen is —183°, nitrogen can be separated from oxygen without difficulty by the fractional evaporation of liquid air. This process has the advantage of yielding a nearly pure gas and is used for some commercial purposes, but the producer-gas process is rather cheaper. Since producer-gas consists chiefly of nitrogen and carbon monoxide, the problem is to remove the latter. This is done by adding steam to the mixture and passing it over a heated catalyst, as described in the account of the HABER-BOSCH process (p. 388). Nitrogen has also been obtained from air by burning hydrogen in it and removing the oxygen as water (p. 391).

Properties.—Nitrogen is a colourless gas without taste or smell; liquid nitrogen, which is also colourless, freezes at —210° and boils at —195°. Nitrogen is only slightly soluble in water: less soluble than is oxygen, but as the partial pressure of nitrogen in the air is nearly four times that of oxygen, water saturated with air contains nearly twice as much nitrogen as oxygen: at 15° a litre contains about 14 c.c. nitrogen and 7 c.c. oxygen. The solubility of nitrogen in organic liquids is also very slight. The gas is a little lighter than air.

At ordinary temperatures nitrogen is a very inert substance. At very high temperatures, at which some dissociation into atoms takes place, it is more active, and the inertness of nitrogen in the cold may be attributed, in part at least, to the stability of its diatomic molecule. The combination with hydrogen or oxygen on heating will be fully discussed shortly (p. 409). Ordinary nitrogen will not combine directly at any temperature with sulphur or the halogens, but many metals, strongly heated in nitrogen, form nitrides.

Active Nitrogen.—In 1910 it was observed by STRUTT that nitrogen at low pressure which had been exposed to a jar-discharge in a vacuum tube to excite the well-known afterglow possessed chemical properties which sharply distinguished it from the ordinary gas. In the case of air and other mixed gases the continuation of the glow after the discharge had been stopped was supposed to be due to the chemical interaction of substances such as nitric oxide and ozone produced by the discharge, but Strutt's observations recalled the behaviour of ozonized oxygen in that the gas leaving the tube had definite chemical properties which persisted until in some minutes it had reverted to the ordinary form.

Subsequent work showed that the presence of traces of oxygen had a pronounced effect on the production of active nitrogen. While not absolutely necessary to its formation a small quantity of oxygen acts as a promoter, but larger concentrations are harmful and 2 per cent is enough to prevent it. A similar effect has been observed with other substances.

Owing to its short life few of the physical properties of active nitrogen can be measured, but it is interesting to note that the spectrum of the glow certainly arises from *molecular* nitrogen. The chemical properties can, however, easily be observed by slowly pumping the gas from the discharge tube where it is generated into an adjacent vessel where it can be exposed to the action of various substances. With sulphur, arsenic, the alkali-metals, zinc, mercury, cadmium, magnesium, and lead direct combination takes place, sometimes with incandescence or flame. Iodine reacts with a blue flame. The carbon compounds mostly yield cyanogen, but methane and hexane give hydrogen cyanide. Yellow phosphorus is converted to red, oxygen and ammonia destroy the glow without reaction. With nitric oxide an unexpected reaction takes place:

$$\text{Active } N + 2NO = NO_2 + N_2.$$

Selenium, carbon, hydrogen, antimony, and ozone are unaffected, but if various salts are exposed to the active nitrogen they begin to phosphoresce.

The nature of active nitrogen is still in doubt. Strutt's original hypothesis was that the gas was simply atomic nitrogen, but the energy available seems insufficient to dissociate the nitrogen molecule. If the molecule of the gas were triatomic, as in ozone, it should be possible to condense it to a liquid, but this has never been accomplished. A likelier view, on the evidence as a whole, is that active nitrogen contains both free atoms and activated molecules.

NITROGEN HYDRIDES.—The hydrides of nitrogen are ammonia, NH_3, hydrazine, N_2H_4, and hydrazoic acid, HN_3. Since the first two are basic compounds and the last an acid, other derivatives also exist, such as ammonium azide, NH_4N_3; but of all these compounds by far the most important is ammonia.

Ammonia, NH_3, is one of the products of decay of animal matter (p. 384), and its odour can frequently be detected in stables and elsewhere. In the laboratory it is usually prepared by the action of a base on an ammonium salt: quicklime and ammonium sulphate are commonly used, with or without the addition of a little water:

$$CaO + (NH_4)_2SO_4 = CaSO_4 + 2NH_3\uparrow + H_2O.$$

Since the gas reacts with calcium chloride, sulphuric acid, or phosphorus pentoxide, some other drying agent must be used, such as quicklime or solid caustic potash.

The preparation of ammonia from atmospheric nitrogen is a great chemical and engineering problem which has been successfully solved only in the last forty or fifty years. The reaction is $N_2+3H_2\rightleftharpoons 2NH_3$, and it has already been shown (p. 123) that the synthesis requires a high pressure. The union of nitrogen and hydrogen is an exothermic reaction, so the yield of ammonia at equilibrium is improved by reducing the temperature, but as a satisfactory reaction velocity can be obtained only at fairly high temperatures, the reaction is carried out at 500° with a catalyst. There are two main processes worked on a commercial scale: the HABER-BOSCH and the CLAUDE, the principal difference lying in the pressure employed.

The Haber-Bosch Process.—This was worked at a large factory at Oppau, near Ludwigshafen-am-Rhein, in Germany, where about 150,000 tons per annum of synthetic nitrogen were produced, while the newer Lunawerke, in Germany, had a capacity of 500,000 tons per annum.   Just before the war of 1939–45 the German production of synthetic nitrogen compounds was about half the world's consumption of nitrogen compounds, including nitrates.   A large plant operates the process at Billingham-on-Tees, in England.   A short description will be given here of the process worked at Oppau; it can be followed out with the help of the simplified flow-sheet opposite.

The great feature of the process is that nothing is wasted.   Besides air and water the raw materials are coke, from the Ruhr coke-ovens, brown coal or lignite, and anhydrite (calcium sulphate) from the Neckar Valley.   The products are aqueous ammonia, ammonium sulphate, nitric acid, calcium nitrate, methyl alcohol, $CH_3.OH$, and urea, CON_2H_4.

The nitrogen and hydrogen are prepared by removing carbon monoxide from producer-gas and water-gas respectively.   This is done by adding steam and passing the gas mixture over a catalyst, when most of the carbon monoxide is oxidized to the dioxide:

$$CO+H_2O\rightarrow CO_2+H_2.$$
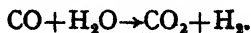
After this operation the carbon dioxide, which comprises some 30 per cent by volume of the gas mixture, is dissolved at 30 atmospheres in water.   Only 1 per cent of carbon monoxide remains, and this is removed by passage through an ammoniacal solution of cuprous chloride.   The gas mixture now consists of nitrogen and hydrogen in nearly the right proportions, though it is sometimes necessary to add a little extra nitrogen from a Linde liquid air plant.   Other

AIR

Cooler, used
for raising steam | NO

NITRIC ACID

WATER | NO

$4NH_3+5O_2 \rightarrow 4NO+6H_2O$

AIR

NH_3

Nitric acid tower

HNO_3

AQUEOUS AMMONIA

NH_3

NH_3 boiled off

Compressor to 200 atmos.

$CO_2 \& NH_3$

ANHYDRITE (Ca SO_4)

AMMONIUM SULPHATE

NH_3 absorbed in water

NH_3 solution

HNO_3

$CO_2+2NH_3 \rightarrow CO(NH_2)_2+H_2O$

UREA

$CO_2 \& NH_3$

CO_2

CO_2

unchanged $N_2 \& H_2$

$N_2+3H_2 \rightarrow 2NH_3$

500°

NH_3 solution

$2NH_4OH+CaSO_4CO_2$

$NH_4)_2SO_4+CO_2+H_2O$

CO_2 CaCO_3

$CaCO_3+2HNO_3 \rightarrow$

$Ca(NO_3)_2+CO_2+H_2O$

CALCIUM NITRATE

Pelton wheel
(power recovered)

CO_2

N_2,H_2

2 stage compressor to 200 atmos.

CO_2

N_2,H_2,CO

CO absorbed in Cu_2Cl_2 solution

Cu_2Cl_2 solution

CO boiled off

CO

CO_2

3 stage compressor to 30 atmos.

NITROGEN (from Linde Plant)

WATER

$CO+H_2$

$CO+H_2O \rightarrow CO_2+H_2$

WATER

$CO+H_2$

$CO+2H_2 \rightarrow CH_3OH$

METHYL ALCOHOL

STEAM

Producer-Gas $CO \& N_2$

$2C+O_2 \rightarrow 2CO$

Water-Gas $CO \& H_2$

$C+H_2O \rightarrow CO+H_2$

AIR

COKE

STEAM

FIG. 105. HABER-BOSCH PROCESS FOR SYNTHETIC AMMONIA (OPPAU PLANT): SIMPLIFIED FLOW-SHEET

large-scale processes for hydrogen production used in ammonia synthesis are described on p. 359. The nitrogen-hydrogen mixture after compression to 200 atmospheres passes into the ammonia converters. These are steel towers 40 feet high and about 3 feet in diameter, containing the catalyst, which is ferric oxide of definite granular structure with small quantities of certain promoters. The temperature of 500° is easily maintained by the heat liberated in the reaction. Only 10 per cent or less of the gas is converted to ammonia at each operation, but the mixture is re-circulated and the ammonia removed by passing it at the same pressure of 200 atmospheres through water. Some of the ammoniacal solution obtained is sold direct, but the rest of the ammonia, which can be obtained from the solution by releasing the pressure and then boiling, is used for three purposes: (1) oxidation to nitric acid; (2) manufacture of ammonium sulphate; (3) manufacture of urea.

1. *Oxidation of Ammonia to Nitric Acid.*—The ammonia is mixed with air or oxygen and passed through towers containing the catalyst, a preparation of ferric oxide, though in other works grids of platinum wire in aluminium tubes are used. With ferric oxide the efficiency is only 70–75 per cent as compared with 95–98 per cent with platinum, but the platinum is expensive and is very easily poisoned. Nitric oxide is formed first, and this is oxidized by more air to nitrogen peroxide, which is absorbed in water which trickles over clay rings. The equations are:

$$4NH_3+5O_2=4NO+6H_2O \qquad 2NO+O_2=2NO_2$$
and
$$4NO_2+2H_2O+O_2=4HNO_3.$$
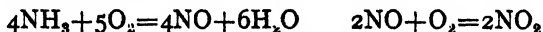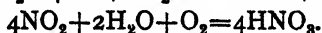
The nitric acid produced is partly sold as such and partly used to make calcium nitrate with the calcium carbonate obtained as a by-product in the manufacture of ammonium sulphate. Smaller quantities are used in the manufacture of ammonium nitrate and of mixed nitrate and phosphate fertilizers.

2. *Ammonium sulphate.*—In order to prepare this substance, so much used as a fertilizer, carbon dioxide, obtained as already described, is passed into a well-stirred suspension of finely-ground anhydrite in water saturated with ammonia. The action is:

$$2NH_3+2H_2O+CaSO_4\downarrow+CO_2=(NH_4)_2SO_4+CaCO_3\downarrow+H_2O,$$
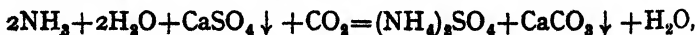
and as calcium carbonate is much less soluble than the sulphate it goes nearly to completion. The solution is filtered, and the ammonium sulphate obtained by evaporation and dried in a centrifugal machine.

3. *Urea.*—This substance, which has the formula $CO(NH_2)_2$, contains 47 per cent of combined nitrogen, and is an excellent fertilizer. Ammonia and carbon dioxide are mixed and compressed

to 200 atmospheres, when they are converted to liquids and react with the formation of ammonium carbamate:

$$CO_2+2NH_3=NH_2.COONH_4.$$
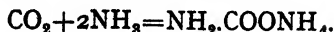
Much heat is evolved, and the carbamate decomposes into urea and water, which, still under pressure, are squirted through a nozzle into a large chamber full of dry air. The urea then falls to the floor as a dry powder, and is removed on conveyors.

$$NH_2.COONH_4=CON_2H_4+H_2O.$$
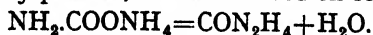
Methyl Alcohol.—We may now return to an earlier stage of the process. The carbon monoxide removed from the gas stream by ammoniacal cuprous chloride is recovered from this solution and used together with some of the water-gas for the manufacture of methyl alcohol. The mixture is compressed and allowed to react on the surface of a catalyst composed of a mixture of zinc oxide and chromium sesquioxide:

$$CO+2H_2=CH_3.OH.$$
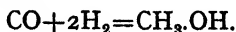
By using as catalyst ferric oxide with a small admixture of alkali, by reducing the speed of the gas stream over the catalyst, and by raising the temperature, it is possible to obtain many other compounds in fair yield; among them isobutyl alcohol, aldehydes, and ketones. The power required throughout the plant is generated from producer-gas, obtained by burning the brown coal to carbon monoxide in an air stream. When the temperature is sufficiently high, steam is substituted for air and water-gas generated instead of producer-gas.

The Claude Process.—This process is worked at numerous factories in France and Belgium. The cost of the hydrogen used in the Haber-Bosch process accounts for about 75 per cent of the cost
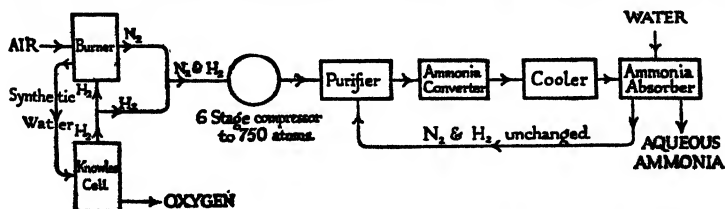
FIG. 106. CLAUDE PROCESS FOR SYNTHETIC AMMONIA: SIMPLIFIED FLOW-SHEET

of the ammonia produced: in the Claude process the hydrogen is made by the electrolysis of water. Some of this hydrogen is burned in air, leaving nitrogen to be used in the ammonia synthesis and synthetic water suitable for the electrolytic cells. The rest of the plant, which works at 750 atmospheres, will be understood from the

diagram. To withstand the enormous pressures the converters are made of special steel, and the catalyst is mounted on a gun breech-block device to allow easy withdrawal for replacement. Many variations of the process are possible; in some the nitrogen is obtained from producer-gas, in others from liquid air.

Several other processes for the manufacture of ammonia from atmospheric nitrogen have at one time been worked, but they are unlikely to make headway against the direct synthetic processes. The SERPEK process for the hydrolysis of aluminium nitride (p. 535) has been abandoned, and the *cyanamide* process (p. 567) is doing no more than hold its own.

Properties.—Ammonia is a colourless gas. At —33° it can be condensed to a liquid freezing at —78°; it is used in refrigerators. It has a strong unmistakable odour and attacks the eyes, and it has a pungent taste. It is considerably lighter than air.

Ammonia is exceedingly soluble in water, and liberates much heat when it dissolves. At 15° and standard pressure 100 gm. of water will take up about 60 gm. of ammonia. In common with other gases with a pronounced affinity for water, ammonia does not obey HENRY's law except in very dilute aqueous solution, that is, the pressure of the gas above the solution is not proportional to its concentration within it. Henry's law, as already explained, is an application of the distribution law to gas-liquid systems, and the reason it is not obeyed by ammonia in water is possibly that the molecular species in the two phases is not entirely the same, and some of the ammonia in solution has combined with hydrogen ions to form ammonium ions. Alternatively the high solubility may be due to hydrogen-bonding between N and O and O and O (and possibly N and N).

All the ammonia can be expelled from its aqueous solutions by boiling, and at very low temperatures, about —77°, hydrates $2NH_3.H_2O$ and $NH_3.H_2O$ have been obtained. Ammonia is freely soluble in most organic liquids.

Ammonia will not burn in the air (unless heated), but in oxygen it burns with a feeble yellow flame, forming (in the absence of a catalyst) nitrogen and water:

$$4NH_3+3O_2=2N_2+6H_2O.$$
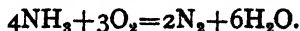
Under carefully controlled conditions and in the presence of a catalyst, preferably platinum, nearly all the ammonia can be con-verted, either by air or oxygen, to nitric oxide, a process used, as already described (p. 390), in the commercial synthesis of nitric acid. Most oxidizing agents, if sufficiently powerful, convert ammonia to nitrogen and water, but some produce oxides of nitrogen or nitric acid. The reaction between ammonia and

chlorine depends on the conditions. .In the gas phase nitrogen is liberated and the chlorine forms first hydrogen chloride, which then reacts with more ammonia to form ammonium chloride:

$$3Cl_2 + 8NH_3 = 6NH_4Cl + N_2.$$
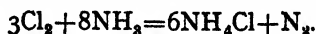
The reaction is accompanied by flashes of light or flame   Under other conditions the dangerously explosive compound nitrogen trichloride may be formed.   Ammonia is detected in aqueous solution by the brown precipitate, or in very dilute solutions the colour, that it produces with NESSLER's solution (p. 515).   It is a powerful donor substance, and, like water, forms addition-compounds with a large number of metallic salts.   These compounds, of which many are described elsewhere, are often of great stability, and the very stable ammonium ion, $NH_4^{\cdot}$, is a combination of the ammonia molecule as donor with the hydrogen ion as acceptor.

Liquid Ammonia as a Solvent.—At atmospheric pressure ammonia can be condensed to a liquid at $-33°$, and it has long been known that the liquid is an excellent solvent for many metallic salts. Reactions in this medium have been intensively studied by GORE in England and by FRANKLIN and his collaborators in America, and there is an ammonia - chemistry that resembles in many interesting points the water-chemistry with which we are familiar. Our views of the nature of reaction have been so much coloured by the predominance of aqueous solutions that the opportunity to investigate a different system is a valuable one; the more so as liquid ammonia is the only solvent other than water whose effect on metallic salts dissolved in it has been thoroughly studied—for the sufficient reason that it is the only non-aqueous solvent in which many of them are appreciably soluble.

The dielectric constant of the liquid is about 22.   If rigorous precautions are taken to exclude water—and this is always important in studying non-aqueous solvents—liquid ammonia is a very poor conductor of electricity.   The few ions present are presumably $NH_4^{\cdot}$ and $NH_2{}'$, formed by dissociation of the ammonia molecule into $H^{\cdot}$ and $NH_2{}'$ and combination of the hydrogen ion with a neutral molecule to form an ammonium ion.   This may be compared with the dissociation of water into $H^{\cdot}$ and OH', and there is reason to suppose that in water also the hydrogen ion is usually attached to at least one water molecule.   The similarity between water and ammonia has indeed often attracted attention; among the most conspicuous points are the high specific heat of ammonia (higher than that of water), its high critical temperature and pressure, its association, and its power of forming molecular compounds with salts analogous to the hydrates.   Still more important

are its solvent action on metallic salts and its power of dissociating them into ions.

Most salts actually conduct the current better when dissolved in ammonia than when dissolved in water, but this is due not to the higher ionizing power of this solvent (which is roughly one-third that of water) but to its lower viscosity, which greatly increases the mobility of the ions.

Salts soluble in water are not always soluble in ammonia, and vice versa.   Halides (except fluorides) are often soluble and carbonates, sulphates, and phosphates sparingly soluble, but metallic oxides and hydroxides do not dissolve at all, except the hydroxides of the alkalis and alkaline earths, and they but slightly.   The course of reactions therefore often differs in water and in ammonia. In ammonia, for example, calcium chloride can be precipitated by mixing a chloride solution with a calcium solution:

$$2NaCl + Ca(NO_3)_2 = 2NaNO_3 + CaCl_2 \downarrow \quad \text{or} \quad 2Cl' + Ca\cdot\cdot \rightarrow CaCl_2 \downarrow .$$
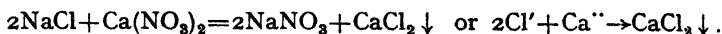
The most instructive classification of solutes is into acids, bases, and salts.   Since the dissociation of liquid ammonia is

$$2NH_3 \rightleftharpoons NH_4\cdot + NH_2',$$

as compared with

$$2H_2O \rightleftharpoons H_3O\cdot + OH',$$

an ammono-acid may be defined as a substance which yields ammonium ions in liquid ammonia solution, and an ammono-base as one which yields amide ions (NH_2').   Since the dissociation of pure liquid ammonia, like that of water, is very slight, it follows that ammono-acids and ammono-bases cannot exist together in solution: the product of their interaction is called an ammono-salt. The equation shows how acetamide, an ammono-acid, neutralizes sodamide, an ammono-base, to produce sodium acetamide, an ammono-salt, and ammonia:

$$CH_3.CO.NH.H + Na.NH_2 = CH_3.CO.NH.Na + NH_3$$
ammono-acid   ammono-base   ammono-salt   ammonia

or $$H\cdot(+NH_3) + NH_2' \rightarrow 2NH_3.$$
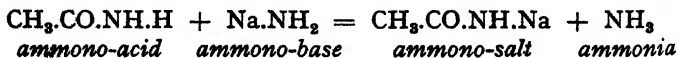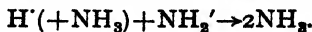
The difference between an ammono-acid and an ammono-base is that the former ionizes $RNH_2 \rightleftharpoons RNH' + H\cdot$, followed by $H\cdot + NH_2 \rightarrow NH_4\cdot$, and the latter ionizes $RNH_2 \rightleftharpoons R\cdot + NH_2'$, just as hydroxylic aquo-acids and aquo-bases correspond with the dissociations $ROH \rightleftharpoons RO' + H\cdot$ and $ROH \rightleftharpoons R\cdot + OH'$.   All soluble ammonium salts are ammono-acids, since they all yield ammonium ions.   Many aquo-oxyacids have their ammono-analogues, thus sulphuric, nitric, and carbonic acids, $SO_2(OH)_2$, $NO_2.OH$, and

$CO(OH)_2$, may be compared with the ammono-acids sulphamide, nitramide, and carbamide, $SO_2(NH_2)_2$, $NO_2.NH_2$, and $CO(NH_2)_2$.

Ammono-acids will dissolve metals, liberating hydrogen:

$$2Na + 2NH_4 \dot{} = 2Na\dot{} + 2NH_3 + H_2\uparrow ;$$
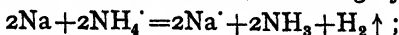
or metallic oxides, yielding a salt, water, and ammonia:

$$Na_2O + 2NH_4\dot{} = 2Na\dot{} + 2NH_3 + H_2O.$$
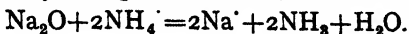
Ammono-bases such as sodamide usually precipitate either a nitride or an amide from ammono-salt solutions, just as caustic alkali precipitates oxides or hydroxides from aqueous solutions. Thus with a solution of a bismuth salt:

$$Bi\dot{}\dot{}\dot{} + 3NH_2' \rightarrow BiN\downarrow + 2NH_3,$$
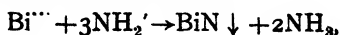
and with a silver salt:

$$Ag\dot{} + NH_2' \rightarrow AgNH_2\downarrow .$$
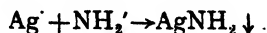
It is considerably more difficult to liberate hydrogen from liquid ammonia than from water, and solutions of the alkali-metals in liquid ammonia can be prepared, though they are not very stable, and decompose after a day or two. The solutions are deep blue in colour and are good conductors of electricity. The cation is the ordinary metal ion, such as $Na\dot{}$ or $Li\dot{}$, possibly associated with ammonia molecules, but the nature of the anion is not immediately obvious. The interesting suggestion has been made that the anion is a free electron, probably solvated, and there is no inherent impossibility in the idea.

THE AMMONIUM SALTS.—Ammonia combines with acids, either in the vapour state or in solution, to form ammonium salts, which contain the ion $NH_4\dot{}$. In these reactions the ammonia acts as donor and the hydrogen ion as acceptor. Though nominally a complex, the ammonium ion does not dissociate into ammonia and hydrogen ion to any great extent. But in the vapour state ammonium salts, which are all volatile, are considerably dissociated into ammonia and acid, the degree of dissociation depending on the temperature, the pressure, and particularly on the volatility of the acid. Thus ammonium carbonate is one of the most volatile and ammonium sulphate one of the least volatile of the common ammonium salts. Similar considerations apply in solution. Ammonium salts with strong acids are slightly hydrolysed and have a faintly acid reaction (owing to the dissociation $NH_4\dot{} \rightarrow NH_3 + H\dot{}$); so that all ammonium solutions, except those containing excess of acid, liberate some ammonia on boiling. If the acid is weak and volatile (e.g. carbonic acid) the salt may be completely decomposed by boiling in water.

The salts of ammonium are often compared with those of the

alkali-metals, since they are colourless (unless the anion is coloured), univalent, and nearly all soluble in water, while they have very little tendency to further complex-formation. Like the salts of potassium, with which they are often isomorphous, ammonium salts usually crystallize anhydrous. The ammonium ion is un-affected by reducing agents, but the stronger oxidizing agents convert it to nitrogen, water, and hydrogen ion, and solutions of ammonium salts of oxidizing anions may liberate nitrogen on boiling, e.g. the nitrite or chlorate. In the solid state such com-pounds are usually explosive.

Among the commoner ammonium salts are the following. Several others are mentioned elsewhere in connection with the acids.

Halides.—The ammonium halides are volatile colourless solids whose volatility decreases with increasing atomic number of the halogen. The fluoride fuses before it sublimes, but the other salts have no melting-point at atmospheric pressure. In the vapour state they are highly dissociated into ammonia and hydrogen halide. In all except the fluoride, a transition-point has been observed corresponding with a difference in crystalline form. The ammonium halides are all freely soluble in water and are also soluble in certain organic solvents, the solubility increasing with increasing atomic number of the halogen, but the fluoride may be an exception to this rule. They all form additive compounds with ammonia.

Ammonium fluoride, NH_4F, is made by subliming a mixture of the chloride or sulphate with excess of sodium fluoride. It is freely soluble in water and is soluble in alcohol. In crystal structure, based on ' hydrogen bonds ' between N and F, it resembles ice (p. 103).

Ammonium chloride, NH_4Cl, is made on a commercial scale from ammonium sulphate and sodium chloride, either by sublimation or in solution. If mixed solutions of these substances are con-centrated, the much less soluble sodium sulphate separates out first and can be removed. The ammonium chloride remaining in the solution is procured by evaporation and purified by recrystalliza-tion or by sublimation. The commercial product usually contains ferric chloride, which colours it yellow, and which may be removed either by sublimation from ammonium phosphate or by recrystal-lization from dilute ammonia. Samples of very high purity were prepared by RICHARDS in the course of his determination of the atomic weight of nitrogen (p. 425). Ammonium chloride is produced whenever hydrogen chloride comes in contact with ammonia in solution or in the vapour phase at low temperatures.

Ammonium chloride has a transition-point at 184°, at which temperature it changes from the body-centred (caesium chloride) structure to the sodium chloride type. On further heating

it readily sublimes without fusion, the vapour pressure reaching 760 mm. at 338°. Measurement of the vapour density shows that even at this temperature dissociation into ammonia and hydrogen chloride is nearly complete, the density being little more than half of that corresponding with NH_4Cl. Since ammonia gas is much lighter than hydrogen chloride it diffuses more rapidly, and it is not difficult, by the use of pipeclay, an asbestos plug, or some other suitable membrane, to effect a partial separation of ammonium chloride vapour. For this reason the purification of the salt by sublimation should always be conducted in a current of ammonia. The claim by BAKER and others that the intensively dried salt does not dissociate has been disproved.

Ammonium chloride is very soluble in water, but much less soluble in alcohol. It is used as a flux in soldering, and in dry batteries, as well as in the Leclanché cell.

Ammonium bromide, NH_4Br, is obtained by the action of bromine on excess of aqueous ammonia. The mixture must be left for a day or two after the vigorous reaction appears to be over, or the product will be contaminated with bromate. The liquid is finally evaporated to dryness on the water-bath.

Ammonium bromide resembles the chloride, but it is slightly less volatile and is more soluble in water and organic liquids. Its transition-temperature is at 138°.

Ammonium iodide, NH_4I, is usually prepared by mixing concentrated solutions of potassium iodide and ammonium sulphate and adding alcohol, which precipitates nearly all the potassium sulphate. It can also be prepared by adding ammonia and then hydrogen peroxide to iodine. It is the least volatile of the ammonium halides, the vapour pressure reaching 760 mm. at about 405°. Its transition-temperature is −18°. In the vapour state not only is there a considerable proportion of undissociated molecules, provided the temperature is not too high, but some association into double molecules takes place. It is deliquescent and exceedingly soluble in water and in some organic liquids.

Ammonium chlorate, NH_4ClO_3, is prepared by concentrating mixed solutions of sodium chlorate and ammonium chloride. The sodium chloride separates out first, and is filtered off. Evaporation of ammonium chlorate solutions is dangerous, as when concentrated they sometimes cause violent explosions. On boiling they yield chlorine and nitrogen. The decomposition of the solid yields in addition water, with some oxygen and ammonium chloride.

Ammonium bromate, NH_4BrO_3, resembles the chlorate, but *ammonium iodate*, NH_4IO_3, is rather stabler. It can be obtained in solution from iodic acid and ammonia, or from ammonium carbonate and barium iodate. It is not very soluble in water:

only about 20 gm. per litre at room temperature. On heating it decomposes into nitrogen, oxygen, iodine, and water, as follows:

$$2NH_4IO_3 = N_2 \uparrow + O_2 \uparrow + I_2 \uparrow + 4H_2O \uparrow .$$
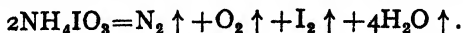
Ammonium perchlorate, NH_4ClO_4, is prepared from ammonium sulphate and barium perchlorate. Unlike potassium perchlorate, it is freely soluble in water. It is, as might be expected, stabler than the chlorate, and on heating yields nitrogen, chlorine, oxygen, and water.

Ammonium carbonate, $(NH_4)_2CO_3$.—The union of carbon dioxide and ammonia in the presence of water can yield a considerable number of products. In the absence of water these gases form *ammonium carbamate*, $NH_2.COONH_4$, an intermediate compound in the synthesis of urea (p. 390). The commercial ammonium carbonate contains the hydrogen carbonate and carbamate as well as the normal salt, but can be freed from these substances by careful washing with aqueous ammonia, in which the normal salt is not very soluble. Even at ordinary temperature the salt slowly decomposes into ammonia and ammonium bicarbonate, and is used as ' smelling salts ': $(NH_4)_2CO_3 = NH_3 \uparrow + (NH_4)HCO_3$. The solutions rapidly lose ammonia to the air, and the evolution of gas from a hot concentrated solution is so brisk that at about 80° it appears to boil. The solutions contain not only bicarbonate but carbamate.

Ammonium bicarbonate, NH_4HCO_3, can be obtained by heating the commercial carbonate or the normal salt with a little water, or by exposing them to the air. It slowly decomposes into ammonia, carbon dioxide, and water, leaving no residue. The fact that ammonium bicarbonate is more soluble than sodium bicarbonate in water makes the SOLVAY process for sodium carbonate manufacture possible.

Ammonium sulphide, $(NH_4)_2S$.—Either this compound or ammonium hydrogen sulphide, $(NH_4)HS$, may result from the union of ammonia with hydrogen sulphide in the absence of water, according to which gas is in excess. The ammonium hydrogen sulphide volatilizes when the product obtained with excess of ammonia at a low temperature is gently warmed. In solution the normal sulphide can be prepared by dividing an ammonia solution into two equal parts, saturating one with hydrogen sulphide and mixing it with the other, but hydrogen sulphide ions (HS') are in any case formed by hydrolysis. Both the solution and the solid are rapidly decomposed on warming.

Ammonium hydrogen sulphide, obtained as above, is also very volatile, the vapour pressure reaching 760 mm. at about 32°. The vapour is almost wholly dissociated into ammonia and hydrogen sulphide.

Solutions of ammonium sulphide, in common with those of other soluble sulphides, have the power of dissolving sulphur, with the formation of polysulphide ions. Ammonium sulphide solutions on exposure to the air absorb oxygen, sulphur being produced, which then combines with the sulphide ions. The first action is:

$$2S'' + O_2 + 2H_2O = 2S + 4OH',$$
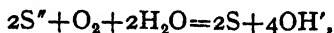
and this is favoured by the acid reaction of ammonium salt solutions, as compared, for example, with those of the alkali-metal salts. The polysulphide solutions are yellow but, if very concentrated, may be red; the yellow solution is a familiar reagent in the laboratory, where it is widely used, in qualitative analysis. Several polysulphides have been prepared in the solid state, among them *ammonium pentasulphide*, $(NH_4)_2S_5$, a yellow crystalline solid obtained by adding sulphur to water through which simultaneous streams of ammonia and hydrogen sulphide are passed. On cooling, the resulting liquid solidifies.

Ammonium sulphate, $(NH_4)_2SO_4$, is made on an enormous scale for use as a fertilizer, for the most part from synthetic ammonia. Either sulphuric acid or anhydrite may be used, as described in the section on synthetic ammonia (p. 390). An alternative source of ammonium sulphate is the ammoniacal liquor from gasworks or coke-ovens, which consists of a very impure aqueous solution of ammonia. Lime is added, and the ammonia, mixed with organic bases, is distilled off into dilute sulphuric acid.

Ammonium sulphate, the salt of a strong and not particularly volatile acid, is one of the stablest and least volatile of the salts of ammonia. It crystallizes without water and is isomorphous with potassium sulphate. On careful heating it loses ammonia and at 320° can be quantitatively converted into the hydrogen sulphate:

$$(NH_4)_2SO_4 = (NH_4)HSO_4 + NH_3 \uparrow.$$
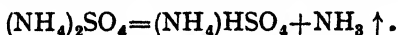
It is extremely soluble in water, and the solubility has a rather low temperature-coefficient.

Ammonium hydrogen sulphate, $(NH_4)HSO_4$, is prepared by carefully heating the normal salt, or by crystallization from solutions of it in dilute sulphuric acid. On stronger heating it yields nitrogen, ammonia, sulphur dioxide, and water. Like the normal sulphate, it is soluble in water but nearly insoluble in alcohol.

Ammonium nitrite, $(NH_4)NO_2$, can be prepared by cautiously evaporating mixed concentrated solutions of ammonium chloride and sodium nitrite, and subliming the product under reduced pressure. It can also be made by passing simultaneous streams of ammonia, nitric oxide, and oxygen into a receiver cooled with cold water. At a temperature of, say, 40° the nitrite can be sublimed

under reduced pressure without decomposition, and thus separated from the less volatile nitrate which usually accompanies it. It is a hygroscopic solid which readily decomposes into nitrogen and water, and is used for preparing nitrogen:

$$NH_4NO_2 = N_2 \uparrow + 2H_2O.$$
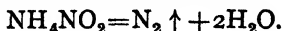
It is freely soluble in water and alcohol. The aqueous solutions give off nitrogen at 50°, or at lower temperatures if the formation of nitrous acid is promoted by the addition of a few drops of a strong acid.

Ammonium nitrate, $(NH_4)NO_3$, is prepared commercially by the action of nitric acid on ammonia. Traces of ammonium nitrate occur in rain, where they have been formed by the interaction of ammonia originating in decaying animal matter and of nitric acid synthesized from air and water by the action of natural electric discharges. Ammonium nitrate is also produced by the reduction of nitric acid by certain metals. The solid exhibits several transition-temperatures connected with changes in the crystalline form, among them one at 32°. At 170° the salt melts, and when further heated decomposes into nitrous oxide and water:

$$(NH_4)NO_3 = N_2O \uparrow + 2H_2O,$$
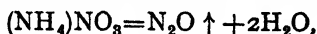
a reaction used for the preparation of this gas. If suddenly and strongly heated, and simultaneously compressed, ammonium nitrate decomposes explosively, producing chiefly nitrogen, oxygen, and water:

$$2(NH_4)NO_3 = 2N_2 \uparrow + O_2 \uparrow + 4H_2O \uparrow .$$
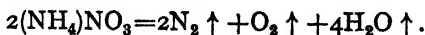
The fused salt is a powerful oxidizing agent which will dissolve many metals, especially if it contains a little ammonium chloride mixed with it. A mixture of ammonium nitrate and aluminium powder can be fired by a detonator, and has been used as an explosive under the name of *ammonal*, while ammonium nitrate has also been used in other explosive mixtures. The memorable explosion at Oppau in Germany in 1922, which caused heavy loss of life and was so violent as to be audible in London, was due to ammonium nitrate.

The salt is exceedingly soluble in water, absorbing much heat when it dissolves: it is also soluble in alcohol.

Ammonium phosphates.—Since ammonia and phosphoric acid are respectively a weak base and a weak acid, a large excess of ammonia is required to produce the hydroxyl ion concentration necessary for the formation of tertiary ammonium phosphate. The ammonium dihydrogen and diammonium hydrogen phosphates can be obtained from solutions prepared by mixing acid and base in

suitable proportions. They are both soluble in water. *Diammonium hydrogen phosphate*, $(NH_4)_2HPO_4$, loses ammonia on heating and gives *ammonium dihydrogen phosphate*, $(NH_4)H_2PO_4$, which on further heating loses all its ammonia and leaves phosphoric acid. *Sodium ammonium hydrogen phosphate*, $Na(NH_4)HPO_4$, 'microcosmic salt,' is described elsewhere (p. 451).

Ammonium peroxide.—By the action of gaseous ammonia on a concentrated solution of hydrogen peroxide in dry ether at a low temperature, say —20°, two peroxides of ammonia can be obtained with the formulae $(NH_4)HO_2$ and $(NH_4)_2O_2$—the latter by continued action of the ammonia. By cooling to —40° they can be isolated as colourless, very unstable solids, which on warming to room temperature rapidly decompose into ammonia and hydrogen peroxide. They may be regarded as the primary and secondary ammonium salts of the weak acid hydrogen peroxide.

AMMINES, AMIDES, IMIDES, AMINES, NITRIDES

Ammines.—It is now generally believed that no definite compounds can be isolated from solutions of the alkali-metals in liquid ammonia, but definite ammines of the alkaline-earth metals have been obtained. Thus *barium hexammine*, $Ba(NH_3)_6$, is produced when ammonia acts on barium at low temperatures. It is stable only at low temperatures, ignites spontaneously in the air, and is decomposed by water.

Amides and Imides.—The amides contain the univalent group NH_2, the imides the bivalent group NH. A large number of these compounds is known, but most inorganic examples are of only theoretical interest. Sodamide and potassamide are of some importance.

Sodamide, $NaNH_2$, is prepared by heating sodium in ammonia gas at about 300°:

$$2Na+2NH_3=2NaNH_2+H_2.$$
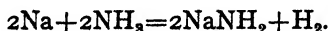
It is, when pure, a colourless solid which melts at 206° to a liquid which decomposes when strongly heated. It is slowly oxidized by the air, even when cold, and when heated in the air burns brilliantly. It reacts with water almost as vigorously as does sodium, producing caustic soda and ammonia:

$$NaNH_2+H_2O=NaOH+NH_3,$$
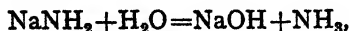
and when heated with carbon produces sodium cyanide, NaCN (p. 453).

Boramide, $B(NH_2)_3$, may be mentioned as an example of an

amide of a non-metal. It is produced by the action of ammonia on boron trichloride:

$$6NH_3 + BCl_3 = B(NH_2)_3 + 3NH_4Cl,$$
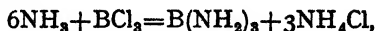
and when heated forms first boron imide, $B_2(NH)_3$, and then boron nitride, BN:

$$2B(NH_2)_3 = B_2(NH)_3 + 3NH_3 \uparrow. \quad B_2(NH)_3 = 2BN + NH_3 \uparrow.$$
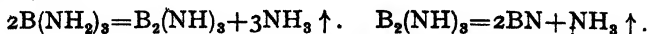
Calcium imide, CaNH, is obtained by passing a mixture of nitrogen and hydrogen over hot calcium.

Silver amide is obtained by the action upon silver nitrate of potassamide dissolved in liquid ammonia:

$$KNH_2 + AgNO_3 = KNO_3 + AgNH_2 \downarrow.$$
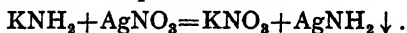
Phospham, PN_2H.—This curious substance, which is probably a polymer $(NP.NH)_n$, is best prepared by heating ammonium chloride with phosphorus pentasulphide. It is a colourless solid unaffected by cold water or cold dilute acids, but decomposed by boiling water into phosphoric acid and ammonia:

$$PN_2H + 4H_2O = H_3PO_4 + 2NH_3.$$
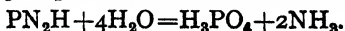
It slowly oxidizes in the air and is decomposed by strong heating.

Chloramine, NH_2Cl.—In this compound one of the hydrogen atoms of the ammonia molecule has been replaced not by a metal, as in sodamide, but by a halogen atom. It is produced by the action of hypochlorites on ammonia in solution:

$$OCl' + NH_3 = NH_2Cl + OH',$$
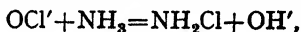
and can be detected in the mixture by its peculiar odour. Distillation at low pressure yields a few drops of chloramine in the distillate as a yellow oil which readily decomposes. The pure substance can be obtained by removing water-vapour from the gas stream with potassium carbonate and condensing the remainder with liquid air. It is a colourless substance, melting at $-60°$ and liable to violent explosion at temperatures but little higher than its melting-point. No similar compounds of the other halogens have been prepared.

Nitrides.—The binary compounds between nitrogen and other elements are called nitrides. The salts of azoimide, or hydrazoic acid, an acid with the formula HN_3, are called *azides*, and are not usually classified with the nitrides, which can be distinguished from them by the fact that the nitrides all liberate ammonia when treated with fused caustic alkalis, and some of them when treated with water, e.g.:

$$Li_3N + 4H_2O = 3LiOH + NH_3 + H_2O,$$
$$BN + 3KOH = K_3BO_3 + NH_3 \uparrow.$$
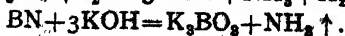
All elements form nitrides *except* the following: the inert gases; Group VIII (*excluding* iron, cobalt, and nickel, which *do* form nitrides), tellurium, bromine. Some of the very rare elements, such as gallium, and a few rare earths, have not been investigated, but from the behaviour of their neighbours in the periodic table it is probable that they would form nitrides. The nitrides of hydrogen, oxygen, carbon, sulphur, phosphorus, and the halogens are discussed separately, and several other nitrides are mentioned under the heading of the second element.

The nitrides can often be prepared by heating the element in nitrogen, or sometimes in ammonia, but a high temperature is usually required. Instead of the element, a mixture of its oxide with a reducing agent such as aluminium or carbon is sometimes used. Some nitrides can be made by heating a suitable compound with another nitride, more easily obtained: lithium and magnesium nitrides, which can be made by union of the elements at a comparatively low temperature, have been used for this purpose.

Hydrazine, $NH_2.NH_2$.—Hydrazine was discovered by CURTIUS in 1887, though the probable existence of such a compound had been foreseen at an earlier date. Small quantities of hydrazine are produced in various reactions, but to obtain a good yield either in the laboratory or on a large scale is not very easy, and hydrazine and its derivatives still command a fairly high price.

The method discovered in 1907 by RASCHIG, and called by his name, is perhaps the best. Aqueous ammonia is boiled with sodium hypochlorite and a little glue. The first product is chloramine, NH_2Cl, and this reacts with more ammonia to form hydrazine chloride, $NH_2.NH_3Cl$:

$$NH_2Cl + NH_3 = NH_2.NH_3Cl.$$
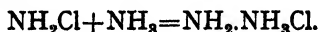
This compound, which is soluble in water, remains in solution, and the liquid is cooled with ice and treated with sulphuric acid, which precipitates the less soluble hydrazine sulphate, $N_2H_4H_2SO_4$, a colourless solid which may be recrystallized from water. Careful working is required or the yield will be poor, as alternative reactions may take place with loss of nitrogen: the object of the glue is to envelop and ' poison ' any traces of heavy-metal ions, that strongly catalyse unwanted reactions.

Hydrazine hydrate, $N_2H_4.H_2O$, is obtained by the action of caustic alkalis on the acid derivatives of hydrazine, but it is difficult to separate it from the resulting solution without considerable loss: resort is had to fractional distillation under reduced, pressure. *Anhydrous hydrazine* is prepared by treating hydrazine sulphate with liquid ammonia, when ammonium sulphate, insoluble in ammonia, is precipitated and removed by filtration. Hydrazine is a

colourless liquid which fumes in the air and attacks cork or rubber; in hot concentrated solution it will corrode glass. It freezes at 0° and boils at 113°. It is soluble in water in all proportions, and forms with it a constant-boiling mixture which boils at about 120°. It is a di-acidic base, and can form salts with one equivalent of an acid or with two. Its first dissociation-constant is about 10^{-6}, so that it is about as weak a base as ammonia, but its second dissociation-constant is only about 10^{-13}, so the dibasic salts of hydrazine are almost entirely hydrolysed in solution. Only one hydrate is known, the monohydrate $N_2H_4.H_2O$, a liquid resembling hydrazine in its properties. The basic properties of the amine groups of hydrazine, like those of ammonia, are presumably due to the power which these groups have of accepting hydrogen ions. Such a compound as hydrazine dichloride ionizes in aqueous solution as follows:

$$Cl.NH_3.NH_3.Cl \rightarrow NH_3.NH_3^{\cdot\cdot} + 2Cl'.$$
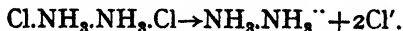
Hydrazine itself is oxidized by the air, and must be kept under hydrogen, while its derivatives are powerful reducing agents from which gaseous nitrogen can easily be liberated. They are rapidly oxidized by the halogens, e.g.:

$$N_2H_5^{\cdot} + 2I_2 = N_2 \uparrow + 4I' + 5H^{\cdot},$$

and in acid solution, in the presence of certain catalysts such as copper salts, will reduce chlorates to chlorides:

$$3N_2H_5^{\cdot} + 2ClO_3' = 3N_2 \uparrow + 2Cl' + 3H^{\cdot} + 6H_2O.$$
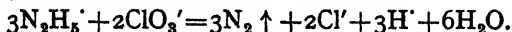
This reaction is used in analysis. Copper solutions are reduced to cuprous oxide, salts of silver, gold, and other electronegative metals to the metal, and ferric to ferrous salts.

Hydrazine is an endothermic compound, and in the presence of platinum black spontaneously decomposes as follows:

$$3N_2H_4 = 4NH_3 + N_2,$$
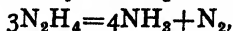
but if a strong base is present the action is:

$$3N_2H_4 = 2NH_3 + 2N_2 + 3H_2.$$
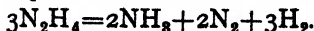
Several of the acid derivatives of hydrazine have been prepared, and the most important is:

Hydrazine sulphate, 'hydrazine hydrosulphate,' $N_2H_4.H_2SO_4$, the commonest hydrazine compound. It is a colourless solid precipitated from cold concentrated hydrazine solutions by sulphates, as it is not very soluble in cold water (about 20 gm. per litre). It is considerably more soluble in hot water, but nearly insoluble in alcohol. It is a stable substance which can be heated to nearly 250° without decomposition.

Hydrazine monochloride, $NH_2.NH_3.Cl$, is made by gently heating the dichloride.

Hydrazine dichloride, $Cl.NH_3.NH_3.Cl$, is usually made in solution from mixed solutions of the sulphate and barium chloride. It is a colourless hygroscopic solid soluble in water and slightly soluble in alcohol.

Hydrazine and its derivatives—such as phenylhydrazine, $C_6H_5.NH.NH_2$, and dinitrophenylhydrazine, $(NO_2)_2C_6H_3.NH.NH_2$— have a limited use in inorganic chemistry as reducing agents, but are much employed in organic chemistry.

Hydroxylamine, NH_2OH.—This compound so much resembles ammonia in its structure that it is generally considered together with the hydrides of nitrogen. It was discovered by Lossen in 1865. Numerous methods for preparing it are known, but they mostly give only a poor yield; the electrolytic method is the best. In this process nitrates are reduced at the cathode in the presence of sulphuric acid. A diaphragm cell is used with a lead or mercury cathode, and the electrolyte must be well cooled. The yield is not very good, and the isolation of the hydroxylamine is difficult, as its salts are soluble in water. The solution is neutralized and heated with acetone, $(CH_3)_2CO$, which reacts with the hydroxylamine to form acetoxime, $(CH_3)_2C:NOH$; this can be extracted with benzene and converted to hydroxylamine chloride, $NH_2OH.Cl$, by treatment with hydrochloric acid. Alternatively a solution of the chloride can be obtained by adding barium chloride to the sulphate solution and filtering. This is then evaporated nearly to dryness under reduced pressure and allowed to crystallize.

Most of the chemical methods of preparation also depend on the reduction of compounds containing nitrogen and oxygen. Lossen's original method was to pass nitric oxide through hydrochloric acid in which tin is dissolving. After a suitable interval the tin is precipitated with hydrogen sulphide and removed, and the filtrate evaporated to dryness, extracted with alcohol, and again taken to dryness, when hydroxylamine chloride remains.

The free base is easily obtained in solution by adding caustic alkali to hydroxylamine salt solutions, but as the resulting solutions are decomposed on boiling, the isolation of the free base is difficult. It was first accomplished in 1890 by adding sodium methoxide $NaOCH_3$, to a solution of hydroxylamine chloride in methyl alcohol:

$$NH_3OH.Cl + NaOCH_3 = NH_2OH + NaCl\downarrow + CH_3OH\uparrow.$$

Sodium chloride, which is nearly insoluble in methyl alcohol, is filtered off, and the alcohol is removed by low-pressure distillation. The hydroxylamine can finally be distilled at low pressure at about 60°, and recrystallized from alcohol, using a freezing-mixture to increase the yield. It is a colourless solid, melting at 33°, which explodes if suddenly heated. It mixes with water in all proportions,

but the solutions are not very stable, especially if impurities are present. In the presence of platinum black they are rapidly decomposed into nitrogen, ammonia, and nitrous oxide, and atmospheric oxidation to nitrous acid and other products also takes place even in the absence of a catalyst. Hydroxylamine is a weak mono-acidic base, weaker than ammonia, and combines with acids to form salts whose cation is $NH_3OH^{\cdot}$, and which are partially hydrolysed in solution; they can be titrated against caustic alkalis with phenolphthalein.

Hydroxylamine most commonly behaves as a weakly basic reducing agent with the structure $NH_2.OH$, the oxidation-products being generally nitrous oxide, N_2O, and water, but sometimes nitrogen, nitric oxide, or even nitric acid. In certain circumstances, however, and notably in strong acid solution, it may behave as an oxide of ammonia, $NH_3 \rightarrow O$, with oxidizing properties. To give an adequate summary of its behaviour it would be necessary to describe its reactions with organic compounds: we may mention here a few of its inorganic reactions.

In neutral or slightly acid solution ferric salts are reduced to ferrous salts, but in concentrated acid solution, or in alkaline suspension, the reverse change takes place. In these reactions nitrous oxide is the principal product of oxidation, ammonia of reduction. Iodine is reduced to iodide except in very concentrated acid solution, when iodides are oxidized to iodine. Cuprous oxide is deposited from FEHLING's solution, and silver from silver salt solutions.

Hydroxylamine chloride, $NH_3OH.Cl$ or $NH_2.OH.HCl$.—This salt is sometimes called hydroxylamine hydrochloride, to express the fact that hydroxylamine forms salts by combination with an acid without the elimination of water: it is a basic anhydride, like ammonia. It is prepared as already described, and is a colourless solid melting at 151° and decomposing on strong heating. It is very soluble in water.

Hydroxylamine sulphate, $(NH_2OH)_2.H_2SO_4$ or $(NH_3OH)_2SO_4$, is obtained by evaporating the chloride to dryness with sulphuric acid in calculated quantity and extracting the residue with alcohol, in which the sulphate is nearly insoluble. It melts with decomposition at about 170° and is very soluble in water.

Azoimide, Hydrazoic acid, Hydrogen azide, HN_3.—Phenyl azide, $C_6H_5.N_3$, was prepared in 1867, but hydrogen azide was not discovered till 1890, when Curtius prepared a small quantity by the action of nitrous acid on hydrazine:

$$N_2H_4 + HNO_2 = N_3H + 2H_2O.$$
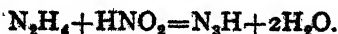
Very numerous reactions have since been discovered by which the acid or its salts can be prepared, though, as with hydrazine and hydroxylamine, it is difficult to get a good yield. CURTIUS's original method gives a fair yield if the acidity is carefully controlled. The oxidation of hydrazine sulphate with a persulphate also gives quite good results, but the best method of all is to heat sodamide to 200° in a current of dry nitrous oxide, when a good yield of sodium azide, NaN_3, is obtained:

$$NaNH_2 + N_2O = NaN_3 + H_2O,$$
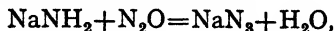
mixed with a little caustic soda produced by hydrolysis of the sodamide. The product is dissolved in water, acidified, and distilled, when the hydrogen azide comes over in the first fraction. The anhydrous substance is obtained by blowing air through its warm aqueous solution, removing water from the air stream by calcium chloride, and condensing the hydrogen azide vapour in liquid air. Hydrogen azide is explosive, and the experiment is dangerous.

Hydrogen azide (this is perhaps the best of the three alternative names for the compound) is a colourless liquid with a nauseous smell, freezing at −80° and boiling at 37°. It frequently explodes when boiled, but the density of the vapour has been measured and found to correspond with the formula HN_3. It mixes with water in all proportions, and the dilute solutions are stable at all temperatures in the absence of catalysts, though the concentrated solutions may explode on heating. The solutions contain a weak monobasic acid; dissociation-constant, say, 2×10^{-5} at 25°, about equal to that of acetic acid. The solutions are very poisonous. Hydrogen azide is easily oxidized to nitrogen, or reduced to ammonia, or, less often, hydrazine. In the presence of platinum black these changes take place simultaneously:

$$3HN_3 = 4N_2 \uparrow + NH_3 \uparrow,$$
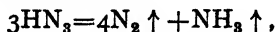
and this reaction can be brought about in solutions of either the acid or its salts. When metals dissolve in the acid solution the hydrogen liberated reduces some of the acid to ammonia, which then forms ammonium azide: compare the production of ammonium nitrate by the action of nitric acid on certain metals. Solutions of hydrazoic acid are also decomposed by acids on boiling, and often oxidize them; thus with hydrochloric acid chlorine is liberated:

$$N_3H + 3H^{\cdot} + 2Cl' = Cl_2 \uparrow + N_2 \uparrow + NH_4^{\cdot}.$$
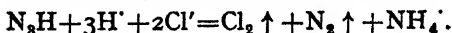
The azides are obtained by acting on hydrazoic acid with bases, and contain the ion N_3'; their solutions have alkaline reactions from hydrolysis. The principal soluble azides are those of the alkali-metals, ammonium, magnesium, and the alkaline-earth metals. They are all explosive, but the alkali-metal azides much

o

less so than those of the heavy metals. Oxidizing agents liberate nitrogen from the azides: e.g. with bromine the action is:

$$Br_2 + 2N_3' = 3N_2 \uparrow + 2Br'.$$
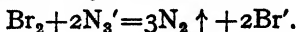
Sodium azide, NaN_3, is prepared by evaporating to dryness the solution prepared from the acid and caustic soda, or from sodamide as already described, and is a colourless solid which can be struck with a hammer with impunity—though it is liable to explode, forming the elements, if heated to about 350°. It is very soluble in water.

Ammonium azide, NH_4N_3, is a colourless volatile solid which if cautiously heated melts at 160° and begins to sublime at about that temperature. If rapidly heated it explodes, yielding nitrogen, hydrogen, and ammonia.

Cupric azide, CuN_6, is a highly explosive substance precipitated from cupric solutions by soluble azides.

Silver azide, AgN_3, is obtained from silver solutions and azide solutions. It can be distinguished from silver chloride by its solubility in warm dilute nitric acid, or even more easily by the violent detonation produced by a sharp blow. It melts at 254°, and explodes at a rather higher temperature. It slowly decomposes into its elements when exposed to light.

Lead azide, PbN_6, resembles silver azide and has been used as a detonator. It exists in two different crystalline forms, one of which is much more dangerously explosive than the other.

Hydrogen azide also forms interesting but unstable compounds in which its hydrogen atom is replaced by a halogen.

Chlorazide, N_3Cl, is a gas produced by the action of hypochlorous acid on azides in acid solution:

$$HN_3 + HOCl = N_3Cl \uparrow + H_2O.$$
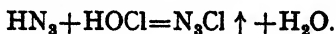
It is a violently explosive substance liable to spontaneous detonation. With alkaline solutions it forms an azide and a hypochlorite. By the action of bromine vapour on silver azide, *bromazide*, N_3Br, is obtained as an orange-red and equally explosive liquid, instantly decomposed by water. *Iodoazide*, N_3I, has been prepared as an explosive yellow solid by the action of iodine in ethereal solution on silver azide: its solutions in water, though unstable, can exist for a short time.

. The structure of hydrazoic acid and its derivatives has now been elucidated with certainty. The old cyclic formula:

$$H-N\underset{\diagdown N}{\overset{\diagup N}{\Big<}} \,\parallel$$
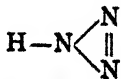
is incorrect, and the formula $N \diagup N = NH$ or $N^- = N^+ = NH$ is in full agreement with the evidence.

OXIDES OF NITROGEN

Heats of Formation.

Nitrous oxide, N_2O,	−19,600	*Nitrogen dioxide,* NO_2	−7,900
		N_2O_4 (gas)	−2,200
		(liquid)	+about 5,000
Nitric oxide, NO,	−21,600	*Nitrogen pentoxide,* N_2O_5 (solid)	+13,000
Nitrogen trioxide, N_2O_3,	−22,200		

HEATS OF FORMATION OF THE OXIDES OF NITROGEN (CALORIES)

As the table shows, the oxides of nitrogen are mostly endothermic compounds, though the exothermic nature of liquid N_2O_4 and solid N_2O_5 should be noted. The trioxide and pentoxide are unstable at ordinary temperatures and are less important than the others.

At high temperatures the stable oxide is nitric oxide, formed from air or any other mixture of oxygen and nitrogen in accordance with the equation:

$$N_2 + O_2 \rightleftharpoons 2NO.$$
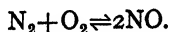
The formation of the oxide is promoted by high temperature, but practically unaffected by changes in pressure. At ordinary temperatures the equilibrium yield of nitric oxide is extremely small, about 0·1 per cent at 1000° and not more than 2 per cent even at 2000°. The reason why no decomposition of nitric oxide can be detected at ordinary temperatures is that the velocity of decomposition only becomes perceptible at about 1200° or over. At very high temperatures better yields can be obtained, and calculation from the VAN'T HOFF isochore gives about 4·5 per cent at 3000°. Still higher temperatures can be reached in the electric arc, and the problem is of great practical importance, since the combination of nitrogen and oxygen is the most obvious, and was for some years the most promising, method of nitrogen fixation. At the temperatures employed the velocity of reaction is very great, but it is absolutely necessary to provide for rapid cooling, as otherwise the nitric oxide decomposes as soon as slightly lower temperatures are reached. At 2000°, for example, the half-life period of nitric oxide is only a fraction of a second, and the equilibrium proportion less than 2 per cent. In all nitric oxide furnaces the gas stream—which may be simply air—is therefore blown at high speed through the arc, usually spread out so as to cover as large an area as possible, and is immediately water-cooled; this is an example of 'freezing the equilibrium.' Nevertheless, heavy losses of nitric oxide must take place during cooling, though the

yields obtained are better than could be expected from a purely thermal equilibrium. The yield of the process as carried out on a large scale with an arc at 3000°–3500° is said to be about 2 per cent, and HABER and KÖNIG reached a yield of no less than 14·5 per cent by working on a small scale and under special conditions. This is considerably more than the equilibrium yield at the temperature employed, and it must be supposed either that the equilibrium is affected by the electric discharge or that some of the reacting gases are dissociated into atoms.

Manufacture of Nitric oxide from Air.—The electrical energy required in industrial practice is about twenty times the heat of formation of the nitric oxide produced, and the factories that worked this process were all situated where cheap electrical power was available, and usually in the neighbourhood of mountain streams which could be adapted to water-power for turning the generators. As the nitric oxide process made no headway against the synthetic ammonia industry, which in time entirely superseded it, only a brief account of the BIRKE-LAND-EYDE process, as formerly worked in Norway, will be given.

FIG. 107. THE BIRKELAND-EYDE FURNACE (DIAGRAMMATIC)

In this furnace the arc is struck between copper U-tubes cooled by a rapid current of water pumped through them. These electrodes lie along one diameter of a circular chamber about seven feet in diameter and made of refractory material pierced with holes for the passage of air. The arc is spread into a semicircle by a large electromagnet whose poles project into the refractory material, as shown in the diagram, and whose coils lie outside the circular chamber. As the current supplied to the electrodes is alternating, while the magnet is fed with direct current, the semicircular arc occupies first one half of the chamber, then the other. Air is drawn through the furnace by suction-pumps connected to the central space, and enters on the outside of the refractory material; as the furnace is circular, the pipes through which the air is carried to the furnace and away from it are not shown in the diagram. It leaves the furnace at 1000° or less.

The combination of nitric oxide and oxygen to form nitrogen

dioxide, which takes place to completion at room temperature, is reversible at higher temperatures:

$$2NO+O_2 \rightleftharpoons 2NO_2.$$
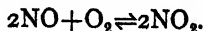
On cooling, the nitric oxide in the gas stream begins to combine at about 620°, and at 140° the action is virtually complete. The first stage of the cooling, down to about 200°, is carried out in boilers where the heat of the gases is used for raising steam, and the gases are then led into large cooling chambers which they leave at about 50° for the towers where they are to be absorbed. Dilute nitric acid trickles down the first few towers, which are filled with granite blocks to increase the area of contact between gas and liquid, and the next tower is supplied with water, while in the last is a solution of sodium carbonate containing some caustic soda to ensure the complete absorption of the nitrogen dioxide. The product of the first towers is nitric acid in concentration up to some 30 per cent, while in the last tower there is produced a mixed nitrate and nitrite solution. Some of the nitric acid was used for the manufacture of calcium nitrate from limestone, and for this reason the salt, which was used as a fertilizer, was sometimes known as ' Norwegian saltpetre,' to distinguish it from Chile saltpetre, an impure sodium nitrate.

Nitrous oxide, N_2O, can be made by reducing nitric acid with stannous chloride and hydrochloric acid in carefully chosen proportions, but is nearly always prepared by heating ammonium nitrate:

$$NH_4NO_3 = N_2O \uparrow + 2H_2O.$$

The gas can be freed from water and from any trace of nitric oxide by passing it through a solution of ferrous sulphate in concentrated sulphuric acid. The ammonium nitrate must be pure and free from chloride, and the heating must be cautiously carried out, for not only is the vessel liable to crack if condensed water falls back on to the hot glass, but the salt is also liable to explode if too strongly heated.

Nitrous oxide is a colourless gas heavier than air, with a peculiar taste and smell. The curious intoxication induced by small quantities led to the name ' laughing gas ' for the substance. Further inhalation leads to insensibility, seldom followed (unless unduly prolonged) by any ill after-effects, and a mixture of the gas with oxygen is still used by dentists as a general anaesthetic. Liquid nitrous oxide freezes at −106° and boils at −90°. The gas is not very soluble in water, and at 15° and atmospheric pressure water will dissolve only about 780 c.c. of nitrous oxide per litre. At low temperatures a hydrate, $N_2O.6H_2O$, can be obtained from the solutions as a colourless solid.

When strongly heated, e.g. to 700° or over, nitrous oxide is decomposed into its elements. It will not burn, and cannot easily be made to combine with oxygen, but will readily support the combustion of most substances that burn in air. Hydrogen burns in it with a large luminous flame, forming water and nitrogen, and charcoal burns in it, forming carbon dioxide and nitrogen. Nitrous oxide can easily be distinguished from oxygen or air by its failure to combine with nitric oxide. It reacts with ammonia when heated, forming nitrogen and water:

$$3N_2O + 2NH_3 = 4N_2 + 3H_2O,$$
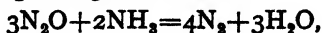
and is fairly stable towards the usual oxidizing or reducing agents.

Nitric oxide, NO.—The synthesis of this compound has already been discussed. It is frequently produced by the action of reducing agents, usually metals, on nitric acid, and in the laboratory copper is generally employed for the purpose. The reaction is usually represented as:

$$3Cu + 8H^{\cdot} + 2NO_3{'} = 3Cu^{\cdot\cdot} + 2NO \uparrow + 4H_2O,$$
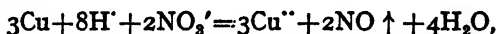
but unless the conditions are carefully regulated, the product is always contaminated with traces of other oxides of nitrogen. A pure gas can be obtained by using cold dilute nitric acid. Care is always necessary in starting the reaction, as it gives out much heat and the velocity increases rapidly with temperature. The best method is to use fairly concentrated nitric acid at first and to dilute it before the evolution of gas becomes too violent. A pure gas can also be obtained by dropping concentrated sulphuric acid on to a solution of sodium nitrite in water; traces of nitrogen dioxide, nitric acid, or hydrogen chloride can be removed by passing the product through water. Whatever method is used, the gas must not be collected till all the air has been driven from the apparatus.

Nitric oxide is a colourless gas, very slightly heavier than air. The liquid freezes at −161° and boils at −150°. At ordinary temperatures it rapidly combines with the oxygen of the air, forming nitrogen dioxide, a brown gas:

$$2NO + O_2 = 2NO_2, 2NO_2 \rightleftharpoons N_2O_4,$$

but without the production of flame. The velocity of the reaction has a small negative temperature-coefficient. Nitric oxide is only slightly soluble in water, but if air or oxygen is also present it forms nitrogen dioxide, which can be completely absorbed. Conductivity measurements on solutions of pure nitric oxide in water show them to contain a very unstable weak acid, perhaps *nitro-hydroxylaminic acid*, $H_2N_2O_3$. Nitric oxide is soluble in solutions of ferrous salts (usually ferrous sulphate), with which it probably

forms a complex ion (Fe.NO)``. The gas is released when the solution is warmed, and can be completely expelled by boiling. Since in some of its reactions nitric oxide shows evidence of unsaturation, it is interesting to find that the vapour density gives no sign of double molecules (see p. 354).

Nitric oxide will support the combustion of certain substances with a great affinity for oxygen. Strongly-burning fragments of phosphorus or charcoal, if plunged into the gas, will continue to burn, leaving nitrogen and forming phosphorus pentoxide and carbon dioxide respectively. On the other hand, burning hydrogen and burning sulphur are extinguished by nitric oxide. However, the gas can be reduced to nitrogen by sparking it with hydrogen, and to hydroxylamine by bubbling it through solutions in which hydrogen is being produced (p. 405).

Nitric oxide combines with the halogens, except iodine, to form compounds such as nitrosyl chloride, $NOCl$. With metallic oxides at different temperatures a variety of products may be formed. Some, such as litharge, PbO, are unaffected, others, such as barium peroxide, form nitrites:

$$BaO_2 + 2NO = Ba(NO_2)_2,$$
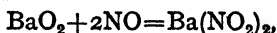
others, such as silver oxide, form the metal and a nitrate:

$$2Ag_2O + NO = 3Ag + AgNO_3,$$
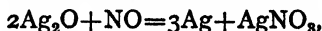
and some lower oxides reduce nitric oxide, forming a higher oxide and nitrogen, e.g. with stannous oxide stannic oxide is produced:

$$2SnO + 2NO = 2SnO_2 + N_2.$$
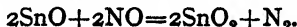
Hydrogen peroxide forms nitrous acid if not in excess:

$$H_2O_2 + 2NO = 2HNO_2,$$

and nitric acid if in excess:

$$3H_2O_2 + 2NO = 2HNO_3 + 2H_2O.$$
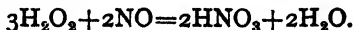
Ferrous hydroxide produces a little hyponitrite:

$$\bullet \quad 2Fe(OH)_2 + 2NO + 2OH' = N_2O_2'' + 2Fe(OH)_3.$$
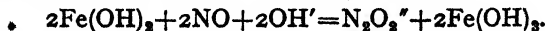
Nitrogen trioxide, N_2O_3, is produced at low temperatures by the union of nitric oxide and nitrogen dioxide:

$$NO + NO_2 \rightleftharpoons N_2O_3,$$

or of nitric oxide with oxygen in quantity insufficient to form the dioxide:

$$4NO + O_2 = 2N_2O_3.$$
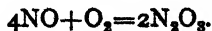
A suitable mixture of nitric oxide and nitrogen dioxide can be obtained by reducing nitric acid of moderate concentration with starch, or a mixture of oxygen with a large excess of nitric oxide

may be employed. When the gas stream is cooled to a sufficiently low temperature the nitrogen trioxide collects as a blue substance which melts at about $-80°$ or $-90°$ and boils with decomposition at $2°$. Solid nitrogen trioxide has also been prepared by the action of the electric arc on liquid air.

At $25°$ C. and 1 atm. the dissociation of the trioxide into nitric oxide and nitrogen dioxide leaves 10 per cent of undecomposed trioxide. The trioxide combines with oxygen, as does nitric oxide, to form nitrogen dioxide, and it is usually supposed to be an inter-mediate product in the oxidation of nitric oxide. It is immediately absorbed by caustic alkali to form a nitrite:

$$N_2O_3 + 2OH' = 2NO_2' + H_2O,$$
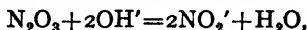
and is indeed the anhydride of nitrous acid.

Nitrogen dioxide, nitrogen 'peroxide,' NO_2 and N_2O_4.—This compound is produced at ordinary temperatures as a brown gas by the action of air or oxygen on nitric oxide; it can also be obtained by distilling lead nitrate, $Pb(NO_3)_2$:

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 \uparrow + O_2 \uparrow,$$
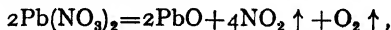
or by reducing nitric acid with arsenic trioxide, As_2O_3. If the gas obtained by any of these processes is passed through a freezing-mixture at about $-20°$ the nitrogen dioxide condenses as nearly colourless crystals which melt at $-10°$, but to remove any nitrogen trioxide it is well to pass oxygen through the liquid.

The colour varies in a striking way with the temperature. The solid is colourless or very pale yellow, and melts without change of colour. At $10°$, however, the liquid is distinctly yellow, and at the boiling-point, $22°$, is orange, while with rising temperature the gas takes on a darker and darker shade of reddish-brown, and at $40°$ is nearly black. Similar colour-changes can be observed in solutions of nitrogen dioxide in solvents such as acetic acid. Vapour-density measurements on the gas, and cryoscopic measurements on the solutions, show that the changes can be accounted for by an internal equilibrium between colourless molecules, N_2O_4, and red-brown molecules, NO_2:

$$2NO_2 \rightleftharpoons N_2O_4.$$
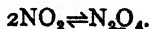
The experimental results are in good agreement with the law of mass-action. The degree of dissociation of the double molecules at atmospheric pressure is 20 per cent at about $27°$, 50 per cent at about $58°$, 90 per cent at about $101°$, and virtually 100 per cent at about $140°$. At higher temperatures nitrogen dioxide begins to decompose into nitric oxide and oxygen, and the colour of the gas consequently becomes paler.

Nitrogen dioxide is much heavier than air. It has a pungent,

disagreeable smell, and is dangerously poisonous. It is completely absorbed by water with the formation of nitrous and nitric acids:

$$2NO_2 + H_2O = HNO_2 + HNO_3,$$
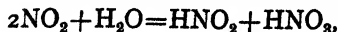
and by caustic alkalis with the formation of nitrites and nitrates. If, however, the nitrous acid concentration rises too high, some nitric oxide is formed:

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$
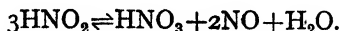
In the presence of air or oxygen in excess, nitric acid is the only product of the action of nitrogen dioxide on water. Nitrogen dioxide is absorbed by concentrated sulphuric acid, and dissolves in concentrated nitric acid to form ' fuming nitric acid.'

Nitrogen dioxide is an oxidizing agent, and under favourable conditions will support combustion. At a high temperature hydrogen reduces it to ammonia, while charcoal and phosphorus, but not sulphur, can be made to burn in the gas. Many metals such as copper or nickel will reduce the gas to nitric oxide when heated in it, themselves forming oxides; other metals form nitrates. Most metallic oxides behave like water and give a mixture of nitrite and nitrate, thus with calcium oxide:

$$2CaO + 4NO_2 = Ca(NO_2)_2 + Ca(NO_3)_2.$$
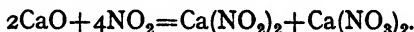
With hydrogen sulphide the products are nitric oxide, sulphur, and water:

$$H_2S + NO_2 = NO + S + H_2O.$$
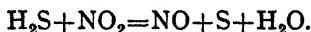
Nitrogen dioxide does not react at ordinary temperatures with the halogens.

Nitrogen pentoxide, N_2O_5, was discovered in 1849 by DEVILLE, who prepared it by the action of chlorine on hot dry silver nitrate:

$$4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 \uparrow + O_2 \uparrow,$$

but is more conveniently obtained by the action of the powerful dehydrating agent phosphorus pentoxide on pure anhydrous nitric acid:

$$2HNO_3 - H_2O = N_2O_5 \uparrow.$$

The nitric acid is first dried by one or two distillations from concentrated sulphuric acid, and is then mixed with a considerable excess of phosphorus pentoxide while the temperature is kept below 0°. The mixture is then cautiously distilled, when the pentoxide collects in the receiver in colourless crystals.

Nitrogen pentoxide is a colourless solid which melts at about 30°, and at room temperature, unless confined in a closed vessel, slowly sublimes without melting, forming nitrogen dioxide and oxygen. It is nitric anhydride, and dissolves in water, forming nitric acid and giving out much heat. It is a powerful oxidizing

and nitrating agent, and in contact with organic substances may give rise to explosions. The decomposition ultimately into nitrogen dioxide and oxygen is a homogeneous unimolecular reaction, and has been the object of much investigation (p. 117). It has recently been shown that the solid is ionic, and represented by the formula $NO_2^{.}.NO^{.}$

NITROGEN OXYHALIDES

Nitrogen forms two series of oxyhalides, the *nitrosyl* halides, such as nitrosyl chloride, NOCl, and the *nitroxyl* or *nitryl* halides, such as nitroxyl chloride, NO_2Cl. To borrow a term from organic chemistry, these are the 'acid chlorides' of nitrous and nitric acids respectively, and on hydrolysis they yield these acids and the hydrogen halide, e.g.:

$$NO_2Cl + H_2O = HNO_3 + HCl.$$
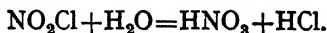
Nitrogen forms no oxyiodides, and the existence of nitroxyl bromide and chloride has been disputed. The nitroxyl compounds are not very stable.

The nitrosyl halides are all gaseous at room temperature. Their melting- and boiling-points are as follows:

	NOF	NOCl	NOBr
Melting-point	$-134°$	$-62°$	$-55°$
Boiling-point	$-56°$	$-6°$	$-2°$

MELTING- AND BOILING-POINTS OF THE NITROSYL HALIDES

Nitrosyl fluoride, NOF, is a colourless gas prepared by the action of nitrosyl chloride on silver fluoride. It is hydrolysed by water, and the solution yields nitric oxide and nitrogen dioxide on warming. Most metals decompose it to form a fluoride and nitric oxide.

Nitrosyl chloride, NOCl, is prepared by the union of nitric oxide and chlorine on a charcoal catalyst at 50°, or by the action of nitric acid on numerous chlorine - containing compounds — hydrogen chloride, ferric chloride, and phosphorus pentachloride have all been employed. The most satisfactory method is to distil a mixture of potassium chloride and nitrosyl bisulphate, $NO.HSO_4$. Nitrosyl chloride is present in *aqua regia*, and is no doubt partly responsible for its solvent properties.

It is an orange gas which must be very strongly heated before it dissociates into nitric oxide and chlorine. It is soluble in water, and its hydrolysis can be repressed if the liquid is strongly acid (e.g. as in *aqua regia*). Heated in nitrosyl chloride, many metals form chlorides and leave nitric oxide, while others form oxides and chlorides and leave nitrogen.

Nitrosyl bromide, NOBr, is prepared by the action of nitric oxide on bromine at low temperatures. Higher oxybromides of nitrogen have been described.

Nitryl fluoride, NO_2F, was discovered in 1905. It is prepared by acting on dinitrogen tetroxide with excess of fluorine at a low temperature and fractionating the product:

$$N_2O_4 + F_2 = 2NO_2.F,$$
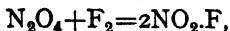
and is a colourless gas with a very pungent odour, which in its chemical activity recalls fluorine: it attacks glass. Nitryl fluoride melts at $-166°$ and boils at $-72°$.

Nitryl chloride, NO_2Cl, is prepared by the combination of nitrogen dioxide and chlorine in a hot tube, or by the action of chlorosulphonic acid, $Cl.SO_2.OH$, on nitric acid:

$$Cl.SO_2.OH + HNO_3 = NO_2Cl + H_2SO_4,$$
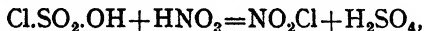
or by mixing nitrosyl chloride with ozone and cooling the product with liquid air:

$$NOCl + O_3 = NO_2Cl + O_2.$$
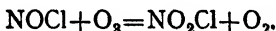
It is a colourless liquid which boils at $-15°$ to form a colourless gas, decomposed by water.

The Oxyacids of Nitrogen

The principal oxyacids of nitrogen are *hyponitrous acid,* $H_2N_2O_2$,

$$\text{nitrous acid,} \qquad HNO_2,$$
$$\text{nitric acid,} \qquad HNO_3,$$

in ascending order of importance. Unstable derivatives of hydronitrous acid, H_2NO_2, and nitrohydroxylaminic acid, $H_2N_2O_3$, have also been prepared.

Hyponitrous acid, $H_2N_2O_2$.—Several methods are known for the preparation of hyponitrites. Nitrites may be reduced either with sodium or magnesium amalgam or electrolytically at a mercury cathode, or nitric oxide may be reduced by ferrous hydroxide. The yield of these processes is usually poor: perhaps ten or twelve per cent. The hyponitrite is isolated from the resulting solution as the insoluble silver salt. The free acid is obtained by suspending the silver salt in ether and adding a solution of hydrogen chloride in ether, then filtering off the silver chloride and evaporating the ethereal solution of the acid to dryness. It is a colourless crystalline solid, very unstable and liable to spontaneous explosion. The aqueous solution liberates nitrous oxide even at room temperature:

$$H_2N_2O_2 = N_2O \uparrow + H_2O.$$

but the acid cannot be made by combination of nitrous oxide and water, and nitrous oxide should consequently not be described as hyponitrous anhydride. Cryoscopic measurements show the acid to exist in double molecules in solution, and it is weak and dibasic. It is a powerful reducing agent, usually forming nitrous acid.

Sodium hyponitrite, $Na_2N_2O_2.5H_2O$, can be obtained in small crystals by the electrolysis of sodium nitrite solutions at a mercury cathode. It can be dehydrated in a vacuum. The solution liberates nitrous oxide on boiling:

$$N_2O_4'' + H_2O = N_2O \uparrow + 2OH',$$
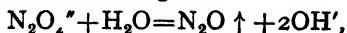
but the solid is stable up to 300°, when it decomposes, attacking even glass and platinum.

Silver hyponitrite, $Ag_2N_2O_2$, is a pale yellow salt precipitated from hyponitrite solutions by silver nitrate. It is unaffected by boiling water, but on heating alone gives silver and nitric oxide, with a little silver nitrate.

Nitrous acid, HNO_2, and the Nitrites.—Nitrous acid has never been isolated, but it can be obtained without difficulty in solution by acidifying cold solutions of nitrites, or, less conveniently, by the action of water on nitrous anhydride, nitrogen trioxide, N_2O_3. The nitrites can be prepared:

(i) from the sodium or potassium salts, prepared by heating the nitrates with or without reducing agents:

$$2KNO_3 = 2KNO_2 + O_2 \uparrow ;$$

(ii) by the action of oxides of nitrogen on aqueous solutions: thus nitrogen dioxide gives a mixture of nitrite and nitrate:

$$2NO_2 + 2OH' = NO_2' + NO_3' + H_2O.$$

A mixture of nitric oxide and dioxide in the right proportions gives pure nitrite:

$$NO + NO_2 + 2OH' = 2NO_2' + H_2O;$$
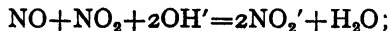
(iii) by reducing nitrates: thus in the presence of lime sulphur dioxide will reduce nitrates to nitrites:

$$NO_3' + SO_2 + CaO = NO_2' + CaSO_4.$$
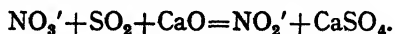
Nitric acid can be partially reduced by nitric oxide, but the action is reversible:

$$2NO + HNO_3 + H_2O \rightleftharpoons 3HNO_2;$$
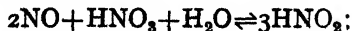
(iv) by oxidizing nitric oxide, either as above with nitric acid, or with hydrogen peroxide or barium dioxide. The oxidation with hydrogen peroxide must be carefully controlled, or nitric acid will be produced.

$$2NO + H_2O_2 = 2HNO_2.$$
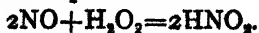
The nitrites are mostly colourless or pale yellow substances soluble in water, but some of the complex nitrites, such as potassium cobaltinitrite (p. 807), are insoluble. Nitrous acid is a weak acid, dissociation-constant about 5×10^{-4}, hence its salts are slightly hydrolysed in solution and have a faint alkaline reaction. Nitrites may have a weak oxidizing or a weak reducing action. The oxidizing action is promoted by acidity, but the peculiarities of the other substance concerned are often more important: thus ferrous salts will reduce nitrites in all circumstances. The general equations are:

$$2NO_2' + 2H^{\cdot} = 2NO + H_2O + O$$

and
$$NO_2' + H_2O = NO_3' + 2H.$$
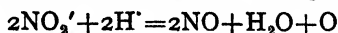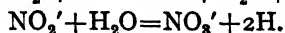
The favourable effect of acidity on the oxidizing powers of nitrites may be attributed either to the hydrogen ions consumed or to the disruptive effect of acids on the nitrous acid molecule, ON.OH, which contains a hydroxyl group united to the elements of nitric oxide, i.e. a nitrosyl group. In certain reactions, mainly involving carbon compounds, nitrous acid can split off a hydroxyl group (not ion) to form water. The other product is called a *nitroso-compound*.

Nitrite solutions are decomposed by boiling; this is a simultaneous oxidation and reduction:

$$3NO_2' + H_2O = NO_3' + 2NO \uparrow + 2OH'.$$
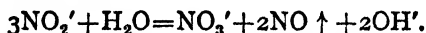
The decomposition is slow in the cold, but can be accelerated by removing the nitric oxide as it is formed, as for instance by passing through the liquid a stream of some indifferent gas, such as nitrogen. Neutral nitrite solutions are stable towards atmospheric oxidation, but this takes place even in the cold if the solution is acid. The small quantities of nitric oxide produced are oxidized by the air to nitrogen dioxide, which, with more air, is absorbed by the solution, producing nitric acid. The total reaction is then:

$$2NO_2' + O_2 = 2NO_3'.$$

Since concentrated nitrous acid solutions decompose, solid nitrites give brown nitrous fumes with concentrated sulphuric acid.

Air, ozone, hydrogen peroxide, bromates, iodates, permanganates, and ceric compounds are among the substances which in suitable circumstances will oxidize nitrites to nitrates. In acid solution hydrogen sulphide is oxidized to sulphur, sulphites to sulphates, and ferrocyanides to ferricyanides. The case of iodine is instructive, for in acid solution iodides are oxidized to iodine, while in neutral or alkaline solution iodine is reduced to an iodide. The equations are:

$$2NO_2' + 2I' + 4H^{\cdot} = 2NO \uparrow + I_2 + 2H_2O$$

and
$$NO_3' + I_2 + H_2O = NO_3' + 2H^{\cdot} + 2I'.$$
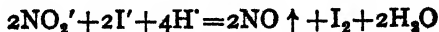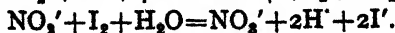
Since nitric oxide, the product of the reduction of nitrous acid, can itself be reduced without much difficulty, the action of vigorous reducing agents on nitrous acid and the nitrites may produce not only nitric oxide but also hydroxylamine, nitrous oxide, nitrogen, or ammonia.

Sodium nitrite, $NaNO_2$, is prepared on a large scale from oxides of nitrogen. The hot mixed gases are passed into caustic soda, and the mixture of nitric oxide and nitrogen dioxide produces a fairly pure salt. Large quantities of sodium nitrite are consumed in the dye industry in the manufacture of diazo-compounds. Sodium nitrite may also be prepared by heating sodium nitrate, but as it is difficult to stop the decomposition exactly at the point required, it is best first to mix the nitrate with a reducing agent. Lead is often used:

$$Pb+NaNO_3=PbO+NaNO_2,$$
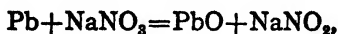
and the nitrite can then be obtained from the product by extracting it with water, in which it is extremely soluble: it absorbs much heat on solution. It melts at $271°$, and on stronger heating decomposes with the formation of sodium oxide, nitrogen, nitric oxide, and sodium nitrate.

Potassium nitrite, KNO_2, is very similar to the sodium salt.

Sodium hydronitrite, Na_2NO_2, is obtained by mixing solutions of sodium and of sodium nitrite in liquid ammonia. It is a yellow solid which reacts violently with water, behaving like a mixture of sodium and sodium nitrite:

$$2Na_2NO_2+2H_2O=H_2\uparrow+2NaOH+2NaNO_2.$$
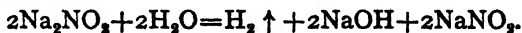
Nitric acid, HNO_3.—Two methods of manufacturing nitric acid on the large scale from atmospheric nitrogen have already been described: the oxidation of ammonia (p. 390), and of synthetic nitric oxide (p. 411). The former now covers the greater part of the world's consumption, but an older process, in which a nitrate is distilled with concentrated sulphuric acid, is still carried out. Potassium nitrate is sometimes preferred to sodium nitrate, as it can more easily be purified by recrystallization. The action is:

$$KNO_3+H_2SO_4=HNO_3\uparrow+KHSO_4,$$
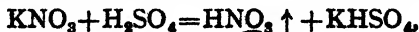
so that half the sulphuric acid is not used, but this action takes place at about $200°$, while the conversion of potassium hydrogen sulphate to potassium sulphate requires a very much higher temperature and a more expensive plant, while some of the nitric acid is decomposed. The stills are made of cast iron, and the water-cooled condensers of special acid-resisting alloy or sometimes of glass. Not all the nitric acid is condensed, and it is necessary to

pass the issuing vapour through towers in which it meets a descending stream of dilute acid. In order to avoid decomposition of the nitric acid, which is perceptible even at 200°, the distillation may be carried out at a lower temperature by reducing the pressure. Nitrogen peroxide dissolved in the product can be removed by blowing air through it. If fuming nitric acid is required, the process can be carried out at a higher temperature. The ' still ' method is now obsolescent, and will doubtless soon be abandoned altogether.
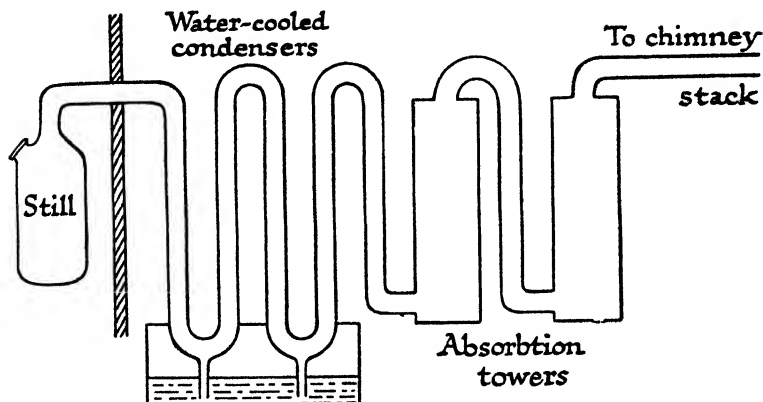
FIG. 108. NITRIC ACID MANUFACTURE (OLD PROCESS)

In the laboratory fuming nitric acid is prepared by distilling concentrated nitric acid with sulphur or starch, when the nitrogen peroxide produced by reduction will be found in the distillate. The commonest impurities in commercial nitric acid are hydrochloric and sulphuric acids. They are removed by adding silver nitrate and barium nitrate, filtering and distilling under reduced pressure.

Properties.—At low temperatures nitric acid is a colourless solid which melts at —41°. Pure nitric acid cannot exist above this temperature, as the liquid is slightly dissociated into nitrogen pentoxide and water. It is soluble in water in all proportions and forms a constant-boiling mixture which boils at 120·5° and contains 68 per cent nitric acid as HNO_3: density 1·41. The acid can be further concentrated by distillation under reduced pressure with concentrated sulphuric acid, and a liquid 100-per-cent HNO_3 by calculation can be prepared by the addition of nitrogen pentoxide, but it contains free nitrogen pentoxide. The density of this acid is 1·52. Hydrates $HNO_3.H_2O$ and $HNO_3.3H_2O$ have been prepared at low temperatures. Concentrated nitric acid has a pungent smell and fumes in the air.

In aqueous solution nitric acid is a strong monobasic acid, but in certain non-aqueous solvents such as methyl alcohol, in which perchloric acid retains its strength, nitric acid is a weak electrolyte. In concentrated aqueous solution, too, it displays peculiarities; it is considerably associated into double molecules, which ionize as follows: $H_2N_2O_6 \rightleftharpoons H_2O + NO_2^{\cdot} + NO_3'$. The nitronium ion $NO_2^{\cdot}$ forms salts such as the perchlorate, and is the active agent in nitration (p. 125).

Nitric acid acts as a *base* in anhydrous HF: $HNO_3 + HF \rightleftharpoons F' + NO_2^{\cdot} + H_2O$.

The oxidizing powers of nitrates are greatly dependent on the presence of water and on the acidity of the solution. Fused sodium and potassium nitrates are very powerful oxidizing agents, used in fusion mixture to bring refractory metals or minerals into solution. The oxidizing power of the nitrate ion in neutral or alkaline solution is, however, very feeble, while concentrated nitric acid is a powerful oxidizing agent, and the fuming acid very powerful indeed. The concentrated acid oxidizes phosphorus to phosphoric acid, sulphur to sulphuric acid, and iodine to iodic acid. Hydrogen chloride is partially converted to chlorine and nitrosyl chloride. A mixture of the two acids in the proportion of one part of nitric acid with three parts of hydrochloric acid is a powerful solvent which will dissolve gold and has been known for centuries under the name of *aqua regia*. Dilute nitric acid will oxidize hydrogen sulphide to sulphur, and ferrous salts to ferric salts on warming. The bright yellow colour produced by the action of concentrated nitric acid on skin, hair, wood, or other organic substances is due to yellow nitro-compounds, e.g. picric acid. The vapour, too, has powerful oxidizing properties; in the vapour state nitric acid is partially dissociated into nitrogen dioxide, oxygen, and water:

$$4HNO_3 \rightleftharpoons 4NO_2 + 2H_2O + O_2,$$
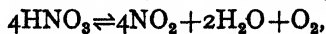
and at high temperatures nitrogen and oxygen make their appearance. Decomposition of the vapour, but not of the liquid phase, is enhanced by exposure to light.

The reduction of nitric acid may yield, according to the circumstances, nitrous or hyponitrous acids, nitrous oxide, nitric oxide, nitrogen dioxide, nitrogen or ammonium or hydroxylamine compounds. The action of the acid on metals is therefore highly complex, and the precise nature of the reactions which take place has been the object of prolonged, though somewhat unfruitful, controversy. Though hydrogen is extremely seldom produced by the action of nitric acid on a metal, yet gaseous hydrogen is unaffected by nitric acid, except in the vapour state and in the presence of a catalyst. There is a considerable

difference between the reducing powers of gaseous and 'nascent' hydrogen. Many metals, such as iron and nickel, become passive in the concentrated acid, a phenomenon which, with iron at least, has been traced to the formation of a film of oxide. Nitric oxide, nitrogen dioxide, nitrites, nitrates, and ammonium compounds are the commonest products of the action of the acid on metals.

The volatility of nitric acid is comparable with that of hydrochloric acid, and when chlorides are heated with nitric acid a balanced action takes place:

$$RCl + HNO_3 \rightleftharpoons RNO_3 + HCl,$$
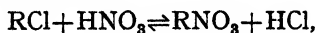
the result depending on which acid is present in excess. On the other hand all nitrates can be completely converted to sulphates by ignition with excess of the much less volatile sulphuric acid.

Nitric acid is used on the large scale in the manufacture of fertilizers, dyestuffs, explosives, and organic chemicals. In the laboratory it is used in the preparation of nitrates and nitro-compounds, as a solvent, and as an oxidizing agent. A solution of a dichromate in concentrated nitric acid is used for cleaning glass apparatus.

Nitrates.—All the simple inorganic nitrates are soluble in water; they may be detected in solution by the ' brown ring ' test (p. 794), or by the white precipitate they give with ' nitron ' (diphenylendo-anilodihydrotriazole). Nitrates are often hydrated, and several nitrates of weak bases (e.g. aluminium nitrate) have never been prepared anhydrous, as hydrolysis takes place on heating.

Nitrates are decomposed by heating. Ammonium nitrate gives nitrous oxide and water, the alkali-metal nitrates give oxygen and a nitrite, others give an oxide (or metal) and oxides of nitrogen, sometimes accompanied by oxygen (e.g. lead nitrate).

Nitrogen Halides

Nitrogen fluoride, NF_3, was discovered in 1928. It is a colourless gas prepared by the electrolysis of fused ammonium hydrogen fluoride, NH_4HF_2. The liquid freezes at $-210°$ and boils at $-119°$. Nitrogen fluoride is quite unlike the chloride and is very stable. It is insoluble in water, and unaffected by water, caustic alkali, glass, mercury, or magnanese dioxide, but it can be decomposed into nitrogen and hydrogen fluoride by sparking with hydrogen.

Nitrogen chloride, NCl_3, was discovered by Dulong in 1811. He was seriously injured (losing an eye and some fingers) in an explosion to which the new substance gave rise, but continued to

investigate it." Since nitrogen chloride is liable to spontaneous detonation, it must never be prepared, without special precautions, in quantities larger than a drop or two.

It is prepared by the action of chlorine or hypochlorites on ammonium salt solutions at a temperature of 30° or 40°. The reactions are:

$$NH_4{}^{\cdot}+3Cl_2=NCl_3+3Cl'+4H^{\cdot}$$

and $\qquad 2NH_4{}^{\cdot}+7OCl'=NCl_3+4Cl'+4H_2O+NO_3{}',$
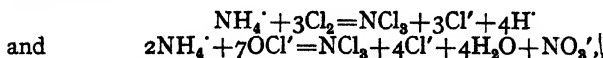
but the yield is always poor, as decomposition into nitrogen and chlorine takes place. The solution must not be alkaline, or chloramine will be produced (see hydrazine, p. 403). The ammonium solution is the first product of the action of chlorine on aqueous ammonia, so if the chlorine is in excess nitrogen chloride may be produced from chlorine and aqueous ammonia.

Nitrogen chloride is sometimes called nitrogen trichloride to distinguish it from chlorazide (p. 408). It is a heavy yellow oily liquid insoluble in cold water, by which, however, it is slowly decomposed with formation of hypochlorous acid and ammonia:

$$NCl_3+3H_2O=NH_3+3HOCl.$$
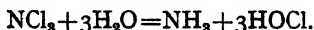
The hypochlorite then oxidizes the ammonia to nitrogen and nitric acid. With hydrochloric acid instead of water the action is:

$$NCl_3+4HCl=3Cl_2\uparrow+NH_4Cl.$$
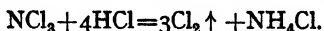
Nitrogen chloride is a covalent compound; it is volatile, evaporating freely in the air, and is soluble in liquids such as benzene or carbon tetrachloride. Many organic substances, however, bring about immediate explosion into nitrogen and chlorine; sunlight and shock have the same effect. The solutions decompose quietly when exposed to light. See also chloramine (p. 402) and chlorazide (p. 408).

Nitrogen bromide has (probably) not been prepared, but a compound $NBr_3.6NH_3$ is obtained by strongly cooling a mixture of bromine vapour and ammonia at low pressure. **Nitrogen iodide,** NI_3, was first prepared in 1931 by the action of ammonia on complex iodides. The name had previously been given to a substance once supposed to have the composition NI_3, but now known to be $N_2H_3I_3$, possibly $NH_3.NI_3$. It is prepared by the action of excess of iodine on ammonia in various solvents, such as aqueous iodides or alcohol, as a black solid insoluble in water. The moist substance is safe, but the dry solid explodes on the slightest provocation, forming nitrogen, iodine, and ammonium iodide. Direct sunlight causes explosion, but if the nitrogen iodide is under water it may decompose quietly.

Nitrogen Sulphides

Ordinary nitrogen will not combine with sulphur, but **nitrogen tetrasulphide,** N_4S_4, can be prepared by passing ammonia into a solution of sulphur dichloride in benzene:

$$16NH_3 + 6S_2Cl_2 = N_4S_4 + 12NH_4Cl\downarrow + 4S_2.$$

The ammonium chloride is filtered off, and evaporation of the solution produces large orange crystals of the tetrasulphide, which can be recrystallized from benzene and further purified by sublimation under reduced pressure. The crystals are almost inodorous: they sublime at about 170° and decompose into the elements if heated to a much higher temperature: rapid heating or shock leads to violent explosion. Nitrogen tetrasulphide is slowly decomposed by water, forming ammonium salts of complex sulphur oxyacids, but it is soluble in many organic liquids, and freezing- and boiling-point measurements on these confirm the formula N_4S_4.

Nitrogen pentasulphide, N_2S_5, is prepared by heating the tetrasulphide with carbon disulphide under pressure, and is a grey solid melting at 11° to form a dense red liquid. It slowly decomposes into sulphur and the tetrasulphide.

The Atomic Weight of Nitrogen

The best determinations of the atomic weight of nitrogen are those of Richards and his collaborators. In the 1907 experiments the weight of silver nitrate obtained from a known weight of silver was determined, and in 1909 they measured the weight of silver chloride obtained from a known weight of ammonium chloride. The atomic weights of silver and chlorine had previously been determined in the same laboratory with extreme accuracy, and these experiments were no less successful. The original papers are of great interest (*J. Amer. Chem. Soc.*, vols. 29 and 31), but here we shall give only a summary of the second series of measurements.

Ammonium chloride was chosen because it can so easily be purified by sublimation. Non-volatile impurities are easily eliminated by passing pure ammonia into pure hydrochloric acid in water, and the most obstinate impurities are amines and other organic compounds. They were oxidized by boiling ammonium sulphate with concentrated sulphuric acid and a little potassium permanganate in a Jena flask until the solution was colourless. After cooling, the salt was dissolved in pure water and the ammonia driven off by warming with freshly-prepared lime. It was absorbed by pure aqueous hydrochloric acid and the chloride recovered from

the solution by evaporation.   All these operations were carried out in enclosed vessels to exclude dust, and to prevent contamination by burner gases all heating was electric.

The ammonium chloride was then purified by sublimation.   This process is apt to introduce new errors, due to interaction with the glass of the vessel at the temperature employed, or excessive diffusion of ammonia, which is considerably lighter than hydrogen chloride, the other product of dissociation of the vapour.   To avoid the first source of error only quartz vessels were used, and the ammonium chloride was sublimed in a stream of ammonia to prevent dissociation, and to remove any free hydrogen chloride which might be present.   The ammonia was obtained by warming a saturated solution of the pure gas in calcium chloride, drying it with lime, and freeing it from solid particles by passing it through cotton-wool and a porcelain diaphragm.
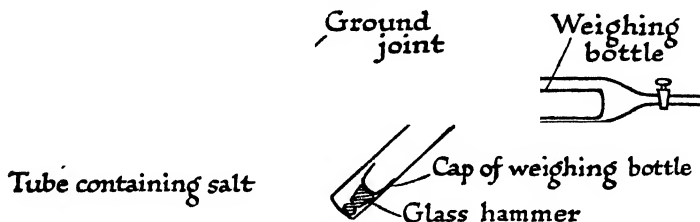
FIG. 109.   THE HARVARD BOTTLING APPARATUS

A second sublimation was then carried out in the vacuum from a Sprengel pump.   The short wide tube in which the salt had been collected was joined to a similar tube by a ground joint at one end, and the two tubes were placed in a wider tube which was then evacuated.   By suitably placed heating coils the ammonium chloride was then sublimed from one tube to the other in which it was to be weighed.   The bottling was carried out in the Harvard bottling apparatus, an ingenious device which makes it possible to weigh without difficulty substances which undergo slight changes of weight when exposed to the air, whether by absorption of water or carbon dioxide, or by oxidation.   It consists of a wide glass tube with a tap at both ends, a ground joint in the middle, and a side-tube to contain the cap of the weighing-bottle and a small glass hammer.   The salt to be weighed, contained in a tube or boat, is placed in the left-hand end of the apparatus, and the weighing-bottle on the right.   The salt can now be finally dried by heating it in a current of nitrogen or any suitable gas or in a vacuum, and by tilting the tube allowed to slide into the weighing-bottle. The tube is then tilted so that the cap of the weighing-bottle falls

into position, where it is secured by a few taps from the glass hammer. The weighing-bottle can then be transferred from the apparatus to the balance, and during the whole operation the salt has been protected from the air.

The weighed ammonium chloride was then dissolved in pure water in a Jena flask. The water for these experiments was obtained by distilling a weak solution of potassium permanganate (to oxidize possible organic impurities) into a platinum condenser. The dilute solution of ammonium chloride was then treated with excess of a dilute solution of silver nitrate which had been prepared by dissolving pure silver in nitric acid and evaporating to dryness. The silver was purified by precipitation as chloride, reduction to the metal with invert sugar and sodium hydroxide, and fusion in a boat of pure lime in an atmosphere of hydrogen to avoid oxidation. The precipitation of silver chloride was always carried out in a darkened room to prevent the change which light brings about in this substance.

The precipitate was brought on to a Gooch crucible and well washed with water. Silver chloride has a very small but nevertheless perceptible solubility in water, and consequently some of it is carried away in the wash-water. The amount thus removed was allowed for by a device due to RICHARDS called the nephelometer. The wash-water is treated with excess of a solution of silver nitrate, and the silver ion concentration is thereby increased to such an extent that the solubility-product of silver chloride is again exceeded and the solution becomes opalescent. By comparing the degree of opalescence with a number of standards derived from solutions of known strength, the concentration in the wash-water can be found and allowed for.

The atomic weight of nitrogen from this research was found to be 14·008; the synthesis of silver nitrate gave 14·013, a difference of one part in two or three thousand.

THE INERT GASES

HELIUM, NEON, ARGON, KRYPTON, XENON, [RADON]

He = 4·003. *Atomic Number*, 2 | Kr = 83·80. *Atomic Number*, 36
Ne =20·183. *Atomic Number*, 10 | Xe =131·30. *Atomic Number*, 54
A =39·944. *Atomic Number*, 18 | [Rn =222.   *Atomic Number*, 86]

History.—In 1785 CAVENDISH caused atmospheric oxygen and nitrogen to combine by means of the electric spark, added an excess of oxygen, and absorbed the resulting oxides of nitrogen in alkali.   He found that however long the sparking was continued and however great an excess of oxygen was used, a small bubble of gas remained which could not be absorbed.   This gas was argon, rediscovered only a century later, but the chemical knowledge of the time was not sufficient to enable Cavendish to understand fully the result of his experiment.

The matter received no further attention till 1894, when LORD RAYLEIGH observed that the density of nitrogen prepared from ammonium nitrite was about half of 1 per cent less than the density of the gas obtained by removing oxygen, water-vapour, and carbon dioxide from air.   The difference, considerably greater than the experimental error, seemed to indicate the presence of a light gas in the first product or a heavy gas in the second.   The second alternative seemed the more probable, and RAYLEIGH and RAMSAY made an experiment to test it.   The oxygen was removed from dry air with hot copper, and the nitrogen with hot magnesium, which combines with it to form magnesium nitride.   A residual gas was obtained unaffected by either treatment and forming nearly 1 per cent of the original volume of air; this new gas was called *argon* (from the Greek, meaning ' lazy,' on account of its remarkable lack of chemical properties).   The story of the discovery, which excited great public interest at the time and is one of the romances of modern chemistry, should be read in *The Discovery of the Rare Gases*, by TRAVERS, who himself took an active part in the work.   Ramsay's *Gases of the Atmosphere* should also be consulted.

It was known that certain scarce minerals, among them cleveite, furnished gaseous nitrogen when heated or when decomposed by powerful solvents, and after the discovery of argon in the air it was thought that it might also be found associated with the nitrogen from these minerals.   Spectroscopic examination of the gas disclosed lines which could be attributed neither to nitrogen nor to

argon, but which had been noticed in 1868 by LOCKYER in the spectrum of the sun's corona, and had been attributed to a new element which he had called *helium*. Meanwhile the fractional distillation of crude liquid argon was successfully accomplished, and yielded besides helium three entirely new gaseous elements, *neon*, *krypton*, and *xenon*. These are all present in air, but in very small quantities, argon being very much more abundant than any of them. A litre of crude argon obtained by removing oxygen, nitrogen, and impurities from air contains the following volumes of other rare gases, in cubic millimetres:

helium, 550; *neon*, 1,600; *krypton*, 5 (?); *xenon*, less than 1.

When it is remembered that a litre contains a million cubic millimetres, the enormous preponderance of argon will be realized. Argon itself is present in air to the extent of 0·93 per cent by volume, so it can scarcely be called a rare gas, since many millions of tons are available in the earth's atmosphere. Large quantities of helium have been obtained from natural gas in certain parts of the United States. These natural gases issue from vents in the ground, and may contain nearly 2 per cent of helium.

Isolation.—The best method for preparing impure argon from air is to remove the oxygen with hot copper and to absorb carbon dioxide and water with caustic alkali followed by concentrated sulphuric acid. The nitrogen is then removed with hot magnesium, leaving a residual gas consisting mostly of argon. Commercial oxygen which has been made by the liquid air process is also a convenient source of argon, of which it may contain as much as 4 per cent. Neon for discharge tubes is obtained by the fractional distillation of liquid air. The air is first separated by fractional distillation into oxygen and nitrogen, the neon and helium being associated with the nitrogen. Since neon boils at —246° and nitrogen at —195°, there is no difficulty in separating the two gases. Traces of nitrogen and oxygen can be removed from the neon by absorbing them in charcoal cooled in liquid air. The charcoal absorbs oxygen and nitrogen far more readily than it absorbs neon. Neon free from helium can be obtained, if required, by solidifying the neon with the help of liquid hydrogen at —253°, leaving the helium, which boils at —269°, uncondensed.

Uses.—Argon, carefully freed from oxygen and nitrogen, is used in filling a certain type of electric lamp, since certain metals used for the filament react even with nitrogen at the very high temperatures reached. Helium has been used in the United States to fill airships: it has the great advantage over hydrogen that it cannot be ignited. It is true that it is twice as heavy as hydrogen, but the lifting power of a gas depends not so much on its density

as on the difference between its density and that of air; the lifting powers of hydrogen and helium are nearly equal. Helium, which has the lowest boiling-point of any known substance—about 4° above the absolute zero—was first liquefied by KAMMERLINGH ONNES in 1907, and solid helium, which melts at less than 1° absolute, has also been prepared. The liquid has been used in research for producing very low temperatures, and a mixture of helium and oxygen is sometimes supplied to deep-sea divers instead of air, as helium is less soluble than nitrogen in the blood. Neon gives a brilliant scarlet in the discharge tube and is widely used in advertising signs.

The advances in pure science which have been made possible by the discovery of the inert gases greatly outweigh any practical benefits which have resulted from that discovery. The identification of helium as a disintegration product of the atoms, first of radioactive and then of other elements, was made possible by Ramsay and Rayleigh's discovery. Neon, too, was the first element to be partially separated into its isotopes. The inert gases are also of the greatest importance, as has already been shown, in the study of the periodic table, and provided the necessary clue to the elucidation of atomic structures. Radon, or radium emanation, is one of the inert gases, but does not, so far as is known, accompany them in detectable traces in the atmosphere.

Some of the physical properties are shown in the table:

	Helium	Neon	Argon	Krypton	Xenon
Atomic Number	2	10	18	36	54
Atomic Weight	4·003	20·183	39·944	83·8	131·3
Melting-point	<1° Abs.	−249°	−188°	−157°	−112°
Boiling-point	4° Abs.	−246°	−186°	−152°	−107°

PHYSICAL PROPERTIES OF THE INERT GASE'

Properties.—The inert gases are all colourless and without taste or smell. They are only slightly soluble in water, but argon and neon are more soluble than is nitrogen. Excluding the gaseous ions which occur in discharge tubes under high potential, it is probably safe to say that they form no compounds. The atoms of the inert gases will not combine even with each other, and the gases are monatomic at all temperatures. The solubility relations in the case of argon, krypton, and xenon are believed to indicate the existence of hydrates ($6H_2O$), and there is nothing unlikely in such a view, for the water molecules might be attached by a new complete ring of electrons round the inert gas atom.

CHAPTER XV

GROUP I

LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, CAESIUM, FRANCIUM, COPPER, SILVER, GOLD

GROUP I occupies one of the extremities of the periodic table. The subgroups are very different in character, for while Subgroup A closely resembles the two typical elements, Subgroup B has but few connections with them.

To show how sharply this group is divided into two by the properties of the elements and their compounds, it is necessary only to quote the standard electrode potentials (here, as throughout the book, on the hydrogen electrode scale) and the melting-points of the elements:

Li
|
Na
| \
K   Cu
| |
Rb   Ag
| |
Cs   Au
|
Fr

Metal	Li	Na	K	Rb	Cs	Cu	Ag	Au
Standard Potential (volts)	−3·02	−2·71	−2·92	−2·92	−2·92	+0·52	+0·80	+1·68
Melting-point	180°	98°	64°	39°	29°	1084°	962°	1064°

The determination of the standard potential cannot be made directly for the alkali-metals (lithium to caesium) because they decompose water: it has been obtained by the use of dilute amalgams of the metals. The figures for gold and copper refer to univalent ions. The comparison shows that copper, silver, and gold are noble metals, while the alkali-metals have low melting-points and decompose water. Sodium, potassium, rubidium, and caesium crystallize in body-centred cubes, copper, silver, and gold in face-centred cubes.

Francium.—In 1931 PAPISH and WAINER claimed to have discovered traces of element No. 87, hitherto known as *eka-caesium*, in the mineral *samarskite*, which also contains the other alkali-metals. By fractional recrystallization of the alums the rubidium and caesium were collected in one part of the sample, but that this material, when examined in the X-ray spectograph, gave lines characteristic of element 87 has not been confirmed. Recently an element with this number (francium, Fr), having β-ray activity and a half-life period of only 21 min., has been detected in the decay products of the α-activity of actinium:

$$^{227}_{89}Ac = {}^{223}_{87}Fr + {}^{4}_{2}He.$$
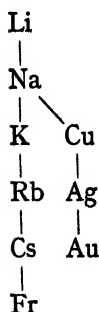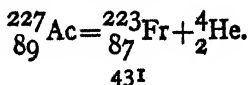
TYPICAL ELEMENTS AND SUBGROUP A

The table gives some fundamental physical properties:

	Li	Na	K	Rb	Cs	Fr
Atomic Number	3	11	19	37	55	87
Atomic Weight	6·940	22·991	39·100	85·48	132·91	(223)
Density of Metal	0·59	0·97	0·97	1·52	1·89	—
Atomic Volume	12	24	45	56	71	—

This is the most homogeneous of all the groups of the periodic table, except Group O, and the chemical properties of the elements and their compounds are very similar. None of them diverges from univalency, and they are always positive in their compounds. Few covalent compounds of the alkali-metals are known, but the ions may form covalent complexes with water of hydration. This is due to the fact that their atomic numbers are all one higher than the atomic number of an inert gas, so that the atom has a very great tendency (as measured by the electrode potential) to lose an electron and become an ion with the very stable inert-gas electron structure. Nearly all their salts are very soluble in water. Potassium, rubidium, and caesium have larger atomic volumes than any other element, and the salts of all the alkali-metals, with one exception, are completely dissociated in solution. Lithium, with a comparatively small atomic volume, is distinguished from the others by a resemblance to magnesium, the second member of the next group, a phenomenon that occurs more than once in the periodic table. It is the only member of the group to form a nitride by direct combination; its carbonate, phosphate, and fluoride are only slightly soluble; its ion shows a feeble tendency to form complexes with ammonia; some of its salts are very soluble in organic solvents, and conductivity measurements show these solutions to contain undissociated ion-pairs, which perhaps occur to some extent in aqueous solution as well. The solid salts of lithium, and to a less degree sodium, show a tendency to take up water of crystallization, and the degree of hydration of the ions decreases from lithium to caesium, which accounts for the observation that the ionic mobility increases from lithium to caesium (p. 153). Rubidium and caesium are chiefly distinguished from the lower members by their greater electropositive character and the power of forming perhalides stable in the solid state.

History.—Sodium and potassium, the two most abundant members of the group, have been known in their compounds from very early times, but were first clearly distinguished by MARGGRAF in the second half of the eighteenth century. Lithium was discovered by ARFVEDSON in 1817. Rubidium and caesium were

discovered by BUNSEN and KIRCHHOFF in 1860 by the method of spectrum analysis: rubidium gives two conspicuous red lines and caesium two blue ones easily distinguished from those of other metals.

Occurrence.—Sodium and potassium are among the most abundant metals on the earth. Only three sources of sodium need be considered: *sodium chloride* or common salt, whether from the sea or from mines, *sodium nitrate* or caliche, from Chile and Peru, and *sodium carbonate* from the deposits at Magadi and elsewhere in East Africa. Potassium is nearly all derived from the Stassfurt deposits of potassium and magnesium salts in Germany. Both sodium and potassium are essential to the life of plants and animals. In countries where salt is scarce it is a valuable commodity, and has been used in savage countries as currency: animals too will travel many miles to obtain it. In many countries—e.g. France or India—salt is taxed or is a monopoly of Government; everybody has to buy it and the tax is difficult to evade. Growing plants require potassium, and it is usually supplied to them in the form of manure if the soil is poor in it, but large quantities of potassium salts are poisonous both to animals and plants. Lithium, though widely diffused in very small quantities, is less common, and is chiefly extracted from two aluminosilicates, *petalite* and *lepidolite*, by fusion with barium carbonate, extraction with hydrochloric acid, evaporation to dryness, and extraction of the resulting lithium chloride with alcohol. Rubidium and caesium are rare metals; the chief source of their salts is the mother liquor remaining from the extraction of the other alkalis. They are contained in carnallite to the extent of about 0·02 per cent RbCl and 0·0002 per cent CsCl. They can be completely precipitated as silicomolybdates (together with a little potassium) from an acid solution of the once recrystallized carnallite. The precipitate is heated in hydrogen chloride, when the molybdenum volatilizes as oxychloride, and the precipitation is repeated. Since practically all the caesium is precipitated first, and is then followed by the rubidium, the isolation of these elements from carnallite is no longer very difficult.

Metals.—It is possible to prepare the alkali-metals by reducing their carbonates with carbon, e.g.:

$$K_2CO_3 + 2C = 2K + 3CO \uparrow,$$
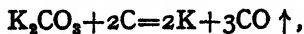
but the process has long been abandoned in favour of electrolytic methods. This is a return to the original method, for in 1807 SIR HUMPHRY DAVY obtained sodium by electrolysing the hydroxide. The activity of the metals towards water precludes the use of solutions for the electrolysis, though lithium has been made by electrolysing a solution of lithium chloride in pyridine. The

hydroxide is used instead of the cheaper chloride, chiefly because it fuses at a far lower temperature. Sodium, and to a less degree potassium, are the only alkali-metals to be produced on a large scale.

Preparation of Sodium.—In the CASTNER process, fused caustic soda is electrolysed in an iron vessel. The negative electrode, consisting of an iron rod, passes up through the base and is fixed in position by solidified caustic soda. The upper end of the cathode is screened by a cylinder of iron wire gauze, immediately above which is an iron tube in which the molten sodium, produced as a result of the electrolysis, is collected and protected from oxidation. The anode consists of a cylinder of nickel, surrounding the cathode (Fig. 110). As the sodium collects, it is

FIG. 110. CASTNER PROCESS FOR THE MANUFACTURE OF SODIUM

removed from time to time with a ladle. Hydrogen (at the cathode) and oxygen (at the anode) are by-products.

In the DOWNS process, fused sodium chloride is electrolysed. The electrolysis cell is a rectangular iron tank lined with refractory earthenware. The anode is made of graphite, while the cathode consists of an iron cylinder surrounding the anode. An iron-gauze cylinder is placed between the anode and the cathode, to prevent the sodium from wandering into the neighbourhood of the chlorine. The cell is filled with fused sodium chloride, more of which is introduced as the electrolysis proceeds. The temperature of the electrolyte is maintained by the resistance it offers to the passage of the current. The sodium liberated at the cathode in the molten condition floats to the surface and runs off through a pipe. The chlorine set free at the anode is used immediately, or collected, liquefied, and stored in cylinders. —

Properties.—All the alkali-metals are soft. When scraped or cut with a knife they show a bright silvery surface which rapidly tarnishes in the air. They are easily extruded as wire from a hand-press. On account of the rapidity with which they are attacked both by the oxygen and by the water-vapour of the air they are always kept under petroleum, but this does not prevent the formation of a film of oxide. In the air they can readily be burned, and in oxygen rubidium and caesium take fire spontaneously.

The metals combine with hydrogen, the halogens, sulphur, phosphorus, and mercury, and lithium combines with nitrogen.

All the alkali-metals react violently with water, forming hydrogen and the hydroxide, e.g.:

$$2K + 2H_2O = 2KOH + H_2 \uparrow.$$
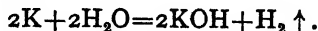
The heat developed is enough to melt the metal (except lithium), which runs about as a globule on the surface of the water, from which it is separated by a cushion of steam and hydrogen. Potassium, rubidium, and caesium grow hot enough to ignite the hydrogen, and explosions sometimes take place. All the metals are very powerful reducing agents, and their action has often to be moderated by the use of a solution in mercury, or amalgam. Freezing-point measurements on these solutions have shown the alkali-metals to be monatomic, and the vapour is also monatomic, though sodium vapour contains some Na_2 molecules: the vapour of sodium is violet, that of potassium green, and that of rubidium blue. The electrical conductivity of the alkali-metals is exceeded only by that of copper, silver, and gold.

Uses.—For some years the chief use of sodium was in the preparation of aluminium, but aluminium is now invariably prepared by electrolysis. Sodium is at present used in the manufacture of sodium peroxide, of sodium cyanide for gold extraction, and of sodamide for the explosives industry. It is also used in sodium lamps for street-lighting, and as a reducing agent in the manufacture of synthetic indigo. An alloy of sodium and potassium, liquid at ordinary temperatures, is used in the photo-electric cells essential in the cinema as intermediaries between speech and the photographic ' sound-track.' The efficacy of such cells depends on the relatively low energy needed to release electrons from alkali-metals.

Potassium is used in radio valves as a ' getter '; that is to say, a fragment of the metal, inserted before the valve is sealed off, improves the vacuum. The silvering on the bulb is due to this cause.

Hydrides.—When the alkali-metals are heated in a stream of dry hydrogen, white crystals of the hydride are formed: the formula is MH, where M is an alkali-metal atom. The hydrides liberate from water twice as much hydrogen as they themselves contain, e.g.:

$$LiH + H_2O = LiOH + H_2 \uparrow.$$

Lithium hydride therefore evolves one-quarter of its own weight of hydrogen, and it has been suggested that hydrogen should be transported in this way. They also react vigorously with the halogens, e.g.:

$$KH + Cl_2 = KCl + HCl.$$
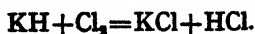
The electrolysis of fused lithium hydride yields lithium at the cathode and hydrogen at the anode. The hydrogen ion in the fused salt must therefore be negatively charged, and has two electrons in association with the proton. This is one of the few cases in which the existence of negatively-charged hydrogen can be proved; the high numerical values of the electrode potentials of the alkali-metals would lead one to expect that in their hydrides the alkali-metals would be positive and the hydrogen negative, and this is found to be correct. The hydrides show every indication of possessing an ionic nature; they have the same crystalline structure as the halides and are insoluble in organic solvents. Hydrogen, in fact, in these compounds plays the part of the halogen.

Oxides.—The following types of oxide are known: M_2O, M_2O_2, MO_2, and possibly M_2O_3. All the alkali-metals except lithium combine with dry oxygen (unless it is ' Baker '-dry, when no action at all takes place) at room temperature: caesium and rubidium with incandescence. The oxides produced are Li_2O, Na_2O_2, KO_2, RbO_2, and CsO_2, so that Li_2O is the only alkali-metal monoxide stable in air; the other alkali-metals will, however, form oxides of the type M_2O if insufficient oxygen for complete combustion is provided. Rubidium monoxide (Rb_2O) is yellow and caesium monoxide orange; the other monoxides are white, but they darken on heating. Lithium monoxide can also be obtained by heating the carbonate; in this respect lithium is unique among the alkali-metals:

$$Li_2CO_3 = Li_2O + CO_2 \uparrow .$$

When heated in hydrogen the monoxides form the hydroxide and hydride:

$$Li_2O + H_2 = LiOH + LiH.$$
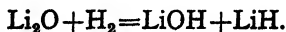
All the alkali-metals, with the probable exception of lithium, form dioxides of the type M_2O_2, but sodium dioxide, usually called *sodium peroxide*, is the only important one. It is made on a large scale by passing sodium on a conveyor through a tunnel at 300°, to which a stream of air, freed from moisture and carbon dioxide, is also admitted; the sodium peroxide is removed at the other end. It is a pale yellow powder usually packed in metal tins, and is a powerful oxidizing agent. It is soluble in water with evolution of heat:

$$Na_2O_2 + 2H_2O \rightleftharpoons 2NaOH + H_2O_2.$$
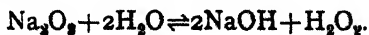
It may be regarded as the disodium salt of the excessively weak acid hydrogen peroxide, and its solutions are consequently much hydrolysed in the sense of the equation above, behaving as though they were alkaline solutions of hydrogen peroxide. Such solutions,

unless carefully freed from dust, are unstable and liberate oxygen, but do so only slowly at low temperatures; they are the best starting-point for the preparation of pure hydrogen peroxide.

Paper or other easily oxidizable matter readily inflames in contact with sodium peroxide, which must therefore be cautiously handled. Under the name of 'oxone' it is used in submarines and other confined spaces for regenerating the air:

$$2Na_2O_2 + 2CO_2 = 2Na_2CO_3 + O_2.$$
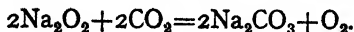
It may also be used in the laboratory as a source of oxygen by treating it with water and allowing the temperature to rise:

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2 \uparrow,$$
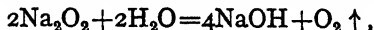
and as a powerful oxidizing agent for decomposing insoluble silicates before analysing them.

The deep-yellow or orange superoxides, MO_2, formed readily by potassium, rubidium, and caesium, contain the ion O_2^-, which with its odd number of electrons (17) confers magnetic properties on the super-oxides. The faint colour of technical sodium peroxide is due to the presence of small amounts of superoxide, NaO_2.

Hydroxides.—These compounds are of the type MOH; the hydroxides of sodium and potassium are of great importance and are produced on the large scale.

PREPARATION OF CAUSTIC SODA.

1. *Electrolytic Methods.*—Two principal types of electrolytic processes are used in the manufacture of caustic soda, viz.:

(a) Those in which the anode and cathode of the cell are separated by a dia-phragm.

(b) Those in which a mercury cathode is used.

In both types sodium chloride solution is the electrolyte.

FIG. III. NELSON CELL FOR THE MANUFACTURE OF CAUSTIC SODA

(a) The NELSON cell is an improvement upon the older Hargreaves-Bird cell. It consists of a U-shaped vessel made of compressed asbestos, and contains the anode, which is a rod of graphite. The

cathode consists of a steel net covering the outer surface of the asbestos walls, which constitute the diaphragm. The whole cell is enclosed in an outer case through which steam can be blown. The cell is supplied with brine, which is kept at a constant level by a self-adjusting device. The brine gradually soaks through the asbestos, where it undergoes electrolysis. Hydrogen and a solution of caustic soda are produced at the cathode, while chlorine appears at the anode and is led off, dried, and compressed into cylinders. The caustic soda solution is run off as required through a pipe in the outer case.

Other cells of a similar kind are in use.

(b) One of the earliest successful cells was the CASTNER-KELLNER, and this is still used in a modified form (Fig. 112). Saturated brine
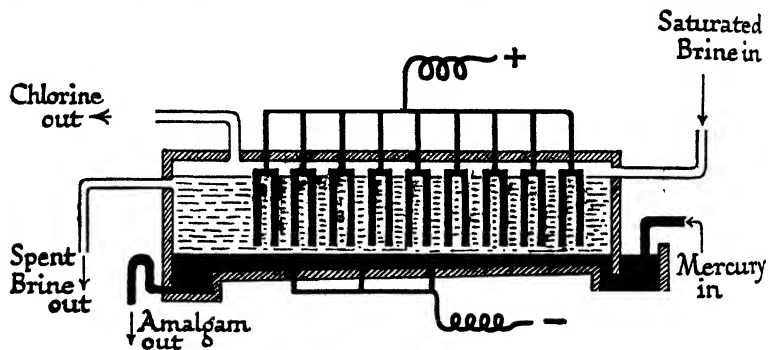
FIG. 112.   CASTNER-KELLNER CELL

is fed into a large rectangular tank, along the slightly sloping floor of which a stream of mercury flows. The mercury is made the cathode, and a series of carbon plates forms the anode. The voltage used is about 120. On electrolysis, chlorine comes off at the anode, escapes through a pipe, and is used directly, or collected, dried, liquefied, and stored. At the cathode, the liberated sodium dissolves in the mercury to form sodium amalgam. This is run off into a lower tank containing water, where the sodium reacts to form sodium hydroxide and hydrogen, and whence the mercury is recirculated through the cell. The hydrogen is collected (generally for direct conversion into hydrogen chloride synthetically), and the solution of sodium hydroxide is evaporated as in the Gossage process. The spent brine leaving the cell is stirred up with more salt to saturate it again, and is then returned through the pipe shown on the right of the diagram.

2. *Preparation from Sodium Carbonate.*—GOSSAGE's method.   In

this process, a 10-per-cent solution of sodium carbonate is boiled with lime:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 + 2NaOH.$$
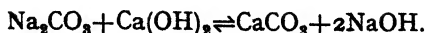
The calcium carbonate is precipitated. As the action is reversible, the working conditions have to be carefully adjusted in order to get the best yield. The solution of caustic soda is filtered off as soon as test portions treated with dilute hydrochloric acid give no carbon dioxide, thus showing that all the sodium carbonate has been decomposed. It is then concentrated in specially constructed vacuum evaporators, heated by steam; the remaining water is driven off by heating in polished cast-iron soda-pots. The temperature required to get rid of the last traces of water is above the melting-point of caustic soda; the latter is therefore left in the molten state and is run off and either sealed up in metal drums or cast into the sticks or pellets used in the laboratory.

Expressed ionically, the action in Gossage's process is:

$$Ca(OH)_2 + CO_3'' \rightleftharpoons CaCO_3 + 2OH'.$$
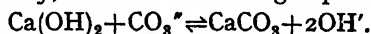
The solubility of calcium carbonate is much less than that of calcium hydroxide, so the reaction goes mainly from left to right. The equilibrium-constant is $\dfrac{[CaCO_3]\,[OH']^2}{[Ca(OH)_2]\,[CO_3'']} = K_1$, and since the concentrations of the lime and calcium carbonate are a constant in their saturated solutions, $\dfrac{[OH']^2}{[CO_3'']} = K_2$. We must now consider the effect of dilution and temperature. In a solution which has reached equilibrium a reduction in the carbonate concentration in the ratio $2 : 1$ will only require a reduction in the hydroxide concentration in the ratio $\sqrt{2} : 1$ if the ratio $\dfrac{[OH']^2}{[CO_3'']}$ is to be kept constant; the efficiency of the process, which is represented by the fraction $\dfrac{[OH']}{[CO_3'']}$, is therefore increased by dilution. This means that the more dilute the sodium carbonate solution with which the lime is treated, the better the percentage yield of caustic soda. On the other hand it is uneconomic to work the plant with very dilute solutions, and as usual a compromise is adopted. The heat involved in the change is very small, so that temperature has no marked effect on the equilibrium; but since a rise in temperature makes the reaction go faster, and consequently increases the output of the plant, the solutions are kept boiling and are well stirred by blowing air through them.

Caustic soda may be made by heating a mixture of sodium carbonate and iron ore (chiefly ferric oxide) in large cylinders, kept

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slowly in rotation about their axis, which is horizontal, so that the mixture is in continual movement. The cylinders are heated by furnace gases streaming through them; the products are sodium ferrite and carbon dioxide, which escapes:

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2 \uparrow .$$
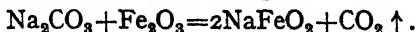
The sodium ferrite is removed when cold and treated with water in settling-tanks, when it produces a solution of caustic soda and ferric oxide, which settles to the bottom:

$$2NaFeO_2 + H_2O = 2NaOH + Fe_2O_3 \downarrow .$$
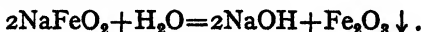
A disadvantage of the process is the expense of maintaining the plant, for the cylinders require frequent renewal.

Purification.—If required pure, sodium and potassium hydroxides are recrystallized from alcohol—in which the salts of these metals are only slightly soluble — and are then said to be ' pure by alcohol.' The commercial samples always contain carbonate, derived from the carbon dioxide of the air, and may contain iron from the evaporating vessels. For volumetric analysis carbonate-free caustic soda solutions can be made by dissolving sodium in water from which the dissolved gases have been removed; this must be done in an apparatus to which the air has no access.

Properties.—The hydroxides of the alkali-metals are white solids, exceedingly soluble in water (except lithium hydroxide, which is moderately soluble); the solution is accompanied by liberation of heat. Lithium hydroxide is the only one from which the oxide can be obtained by heating, and a high temperature is necessary before any decomposition is observed:

$$2LiOH = Li_2O + H_2O \uparrow .$$

They are called ' caustic alkalis.' The word alkali is derived from an Arabic word meaning ' the ash,' since the Arabian chemists were acquainted with the fact that a basic substance (chiefly potassium carbonate) is contained in wood-ash. It was extracted with water and obtained by evaporating the solution, from which impurities had been allowed to settle. The evaporation was carried out in pots: hence the name ' potash,' from which the word potassium is derived.

The hydroxides of all the alkali-metals are strong bases, fully dissociated in solution. Caustic soda and potash are commonly used in the laboratory when a source of hydroxyl ions is required, as in the precipitation of metallic hydroxides. They are also used for removing carbon dioxide from air or other gas mixture— potassium hydroxide is the more suitable for this purpose, since the bicarbonate produced in the reaction is more soluble than

sodium bicarbonate and therefore does not so easily choke the tubes of the apparatus:

$$KOH+CO_2=KHCO_3.$$
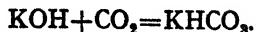
The principal use of caustic soda in industry is the manufacture of soap from oils and fats; for soft soaps potash is used instead of soda. Caustic soda is also used in the preparation of the alizarin dyes, in the mercerization of cotton, and in the paper trade. It is a good cleansing fluid for the removal of grease, with which it often forms a soluble soap; for this reason the solution feels slimy between the fingers from the soap produced from the natural grease. In biological laboratories caustic soda solution is used for removing the flesh from skeletons of specimens: the process takes place rapidly in the boiling liquid. Fused caustic alkalis attack glass.

Although the alkaline hydroxides are regarded as typical strong bases, hydrogen can under certain circumstances be liberated from them by metals. Fused caustic potash dissolves potassium with the liberation of hydrogen:

$$2KOH+2K=2K_2O+H_2\uparrow,$$
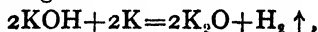
and aluminium is readily soluble in aqueous solutions of caustic soda, forming an aluminate and hydrogen:

$$2Al+2H_2O+2OH'=2AlO_2'+3H_2\uparrow.$$
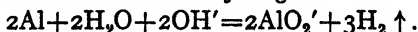
These are reactions in which the old definition of an acid as ' a substance containing hydrogen that can be replaced by a metal ' breaks down; it is better to define an acid as ' a substance which yields hydrogen ions in solution.'

Carbonates.—Sodium carbonate is now manufactured almost entirely by the ammonia-soda, or SOLVAY process. In this process sodium bicarbonate is precipitated from a mixed solution of sodium chloride and ammonium bicarbonate, since it is the least soluble salt present in the system:

$$NaCl+NH_4.HCO_3\rightleftharpoons NH_4Cl+$$
$$NaHCO_3\downarrow.$$

The mixed solution is prepared by saturating brine first with ammonia, then with carbon dioxide, and the process can only be successfully worked in such places as Cheshire where a cheap supply of brine is available. The brine trickles down a tower in which

FIG. 113. UPPER PART OF AMMONIA ABSORBER

ammonia, which enters at the bottom, is made to stream through it by a series of serrated umbrella-shaped metal baffles called

'mushrooms,' so arranged as to divide the gas into a number of small streams of bubbles. The gas leaves at the top, while the liquid, which is a mixed solution of sodium chloride and ammonium hydroxide, passes out at the bottom. It is run through a number of settling-tanks, in which impurities are deposited, and is then pumped into carbonators, where it is saturated with carbon dioxide. These differ in different factories, and may consist of either a tower or a series of smaller vessels. Heat is evolved in the reaction, and since a rise in temperature increases the solubility of sodium bicarbonate, the carbonators are cooled by streams of water. The carbon dioxide is obtained by heating limestone in a kiln:

$$CaCO_3 = CaO + CO_2 \uparrow.$$

The carbonators are so arranged that the solution leaving them has reached equilibrium and carries in suspension all the sodium
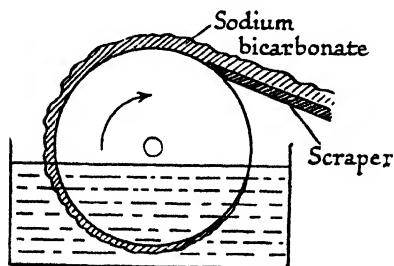
FIG 114. FILTER FOR SODIUM BICARBONATE

bicarbonate that can be precipitated from it. It then passes to the filters, which are made of flannel stretched on cylindrical frames nearly half submerged in the solution and kept in slow rotation. A vacuum is maintained on the inside, and the bicarbonate sticks to the flannel and is removed by a scraper. When the filter becomes clogged after much use, it can be cleaned by blowing air through it from the inside.

The sodium bicarbonate is heated in furnaces, and the sodium carbonate produced is packed in bags and sold. The carbon dioxide returns to the carbonators, after passing through a washer to recover any ammonia which may have been carried away with the bicarbonate, whose decomposition is represented by the equation:

$$2NaHCO_3 = Na_2CO_3 + CO_2 \uparrow + H_2O \uparrow.$$
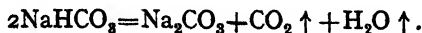
The filtrate consists chiefly of a solution of ammonium chloride, which must not be wasted; the ammonia is recovered from it by adding lime and heating with steam. The lime is derived from the lime-kilns, and the reaction is:

$$NH_4^{\cdot} + OH' = NH_3 \uparrow + H_2O.$$
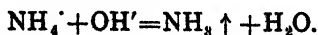
The residue of the process, or 'spent liquor,' is a solution of calcium chloride, for which only a very limited market was formerly

available, but which now has many uses. The whole process is an excellent example of how economy is attained in manufacture by recovering the intermediate substances: for that reason a simplified ' flow-sheet ' is shown (p. 444), on which the movements of the various substances through the plant are represented. The raw materials are sodium chloride and calcium carbonate, the product sodium carbonate, and the waste product calcium chloride. The *net* reaction can therefore be represented by the equation:

$$2NaCl + CaCO_3 = Na_2CO_3 + CaCl_2,$$
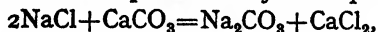
but small amounts of ammonia lost in the process have to be made good. The sodium carbonate made by this process is about 99 per cent pure, the chief impurities being sodium chloride and water.

General Properties.—The carbonates of the alkali-metals are white crystalline solids. Lithium carbonate differs from the others in being only slightly soluble and in liberating carbon dioxide on strong heating. Sodium carbonate forms several hydrates; washing soda is $Na_2CO_3.10H_2O$, and a hydrate, $Na_2CO_3.H_2O$, is formed from washing soda in dry air by the loss of water. The anhydrous carbonate is used in making up solutions for volumetric analysis, and in gravimetric analysis insoluble substances are often fused with sodium carbonate (to which potassium nitrate is sometimes added to lower the melting-point), for the purpose of bringing them into solution. In industry, sodium carbonate is used in the manufacture of glass and paper, and for softening water: considerable quantities are also used in the manufacture of washing powders, which usually consist of an intimate mixture of sodium carbonate and soap, to which a bleaching agent such as a perborate is sometimes added.

On account of the apparent weakness of carbonic acid (*q.v.*), solutions of carbonates have a pronounced alkaline reaction, produced by hydrolysis.

Sodium bicarbonate, or sodium hydrogen carbonate, $NaHCO_3$, is a white solid, not very soluble in water, and is the direct product of the Solvay process. On heating, it liberates carbon dioxide:

$$2NaHCO_3 = Na_2CO_3 + CO_2 \uparrow + H_2O \uparrow,$$

and is therefore used as a constituent of baking-powder. Its solutions are nearly neutral, and the substance is used as a medicine; the acid secretions of the stomach decompose it to form carbon dioxide. A solution of sodium bicarbonate is used to free carbon dioxide, prepared from marble and hydrochloric acid, from traces of the acid; sodium carbonate cannot be used, since its solutions absorb carbon dioxide:

$$CO_2'' + CO_2 + H_2O = 2HCO_3'.$$
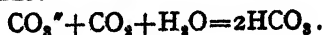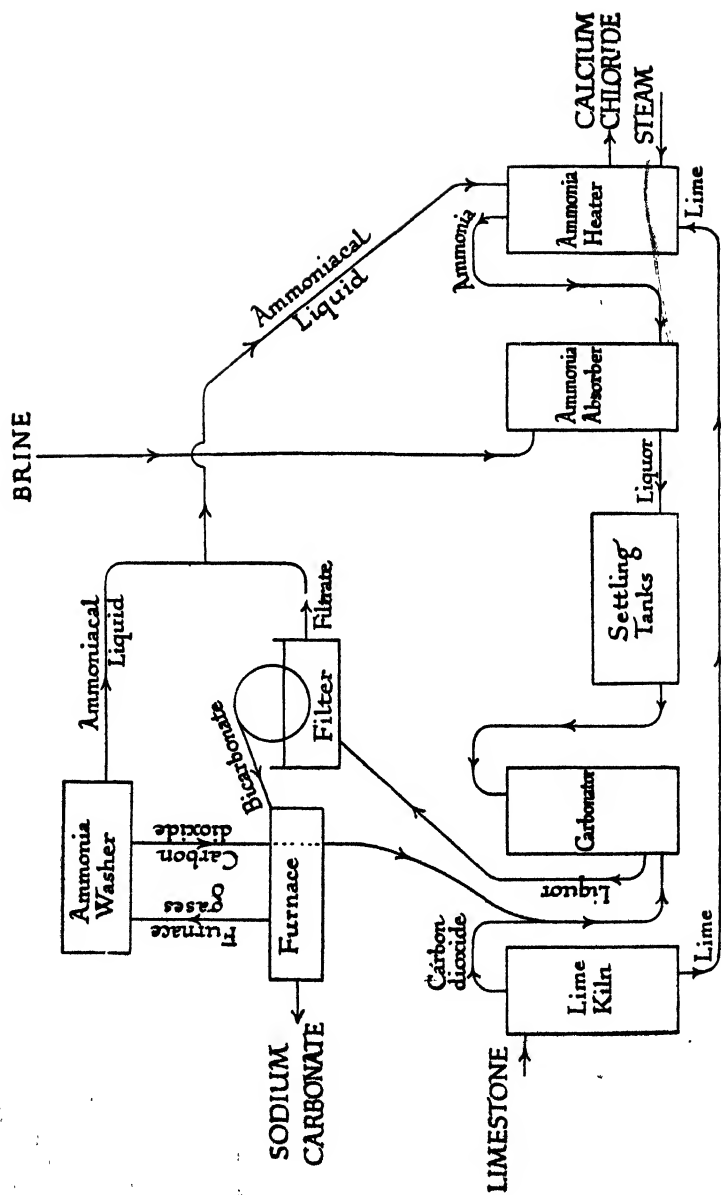
FIG. 115 SOLVAY PROCESS: FLOW-SHEET (SIMPLIFIED)

Potassium carbonate cannot be made by the Solvay process, because potassium bicarbonate is too easily soluble in water. The two principal sources of the salt are (*a*) carnallite from the Stassfurt deposits, and (*b*) beet-sugar molasses, which is mixed with lime, evaporated to dryness, charred, and extracted with water.

In the carnallite process, the carnallite is first melted and then allowed to cool, when potassium chloride crystallizes out and is removed. A concentrated solution of the potassium chloride is made and this is mixed with hydrated magnesium carbonate. On passing a stream of carbon dioxide through the liquid a precipitate of a double salt, $KHCO_3.MgCO_3.4H_2O$, is obtained:

$$3(MgCO_3.3H_2O)+2KCl+CO_2=2(KHCO_3.MgCO_3.4H_2O)+MgCl_2.$$
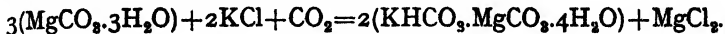
This solid is removed and treated with magnesium oxide, when the hydrated magnesium carbonate is re-formed and potassium carbonate left in solution:

$$2(KHCO_3.MgCO_3.4H_2O)+MgO=3(MgCO_3.3H_2O)+K_2CO_3.$$

After filtration, the solution of potassium carbonate is evaporated to crystallization.

Potassium carbonate is a white deliquescent solid which crystallizes with not more than two molecules of water of crystallization. It is sometimes used as a desiccating agent. ' Commercially pure ' potassium carbonate is commonly known as *pearl-ash*.

Chlorides.—The chlorides of the alkali-metals are white solids with the general formula MCl; they are soluble in water. All the halides of the alkali-metals have the sodium chloride structure, except the chloride, bromide, and iodide of caesium, which have a body-centred lattice. With the exception of lithium and perhaps sodium chloride, none of the alkali-metal chlorides forms hydrates. The solubility of sodium chloride in water is only slightly affected by change of temperature, whereas the other chlorides are all much more soluble in hot water than in cold.

Sodium chloride, NaCl, common salt, or simply ' salt,' occurs in the sea and in enormous subterranean deposits in Austria (*Salzburg* means ' salt town '), Spain, Poland, Siberia, and other parts of the world. In Great Britain the principal salt mines are in Cheshire and at Droitwich. The salt is now generally obtained from these mines by allowing water to penetrate into the galleries and pumping it out as brine when it is nearly saturated with salt. The proportion of sodium chloride in sea-water varies considerably in different parts. The Baltic and the Black Sea contain less than 1 per cent, the Atlantic Ocean rather more, the Dead Sea about 9 per cent, together with 9 per cent magnesium chloride, and the Salt Lake of Utah more still. Large quantities of sodium chloride are

extracted from sea-water in either very cold or very sunny climates. In very cold countries such as Russia the water is removed by freezing, leaving concentrated brine from which the salt can be obtained by evaporation; in sunny climates, such as that of southern France, the water is evaporated by the sun's heat. The predominance of sodium chloride over potassium chloride in sea-water is partly due to the fact that the potassium salt is much more readily adsorbed into the soil.

At 10° a saturated solution contains 35·8 gm. salt per 100 gm. water. In the laboratory sodium chloride is purified by passing hydrogen chloride gas into a saturated solution; this precipitates most of the salt and leaves the impurities in the solution. The action of the hydrogen chloride is twofold: in addition to the common ion effect on the solubility it withdraws water for the hydration of the hydrogen and chlorine ions.

Salt is slightly hygroscopic, and has a tendency to form lumps. This is prevented in some table salts by the addition of small quantities of calcium phosphate, made by heating bones; salt treated in this way remains in fine grains and ' runs ' better than the pure substance.

Sodium chloride, and sodium nitrate from the South American caliche deposits, are the largest sources of sodium compounds. Sodium chloride is also used as a source of chlorine and hydrochloric acid.

Potassium chloride, KCl, was formerly obtained from sea-water, but the chief source is now the Stassfurt deposit in Germany, supposed to be the remains of an inland sea. Among other salts the stratified deposits contain an immense layer of carnallite, $KCl.MgCl_2.6H_2O$, from which potassium chloride of varying states of purity is prepared by a series of crystallizations and washings. In properties it resembles sodium chloride; it is less soluble than sodium chloride in cold water (31·0 gm. per 100 gm. water at 10°), but more soluble in hot water.

Lithium chloride, LiCl, differs from the other alkali-metal chlorides in being quite soluble in such organic liquids as the lower alcohols, phenol, acetone, glycerol, and pyridine. Examination of these solutions by conductivity and other methods shows them to contain complex ions and probably undissociated molecules. On evaporation to dryness in air, an aqueous solution of lithium chloride leaves a slightly alkaline residue:

$$LiCl + H_2O \rightleftharpoons LiOH + HCl \uparrow,$$

and this hydrolysis indicates that lithium hydroxide is perhaps not a completely dissociated base. This reaction does not take place with the other alkali-metal halides.

Rubidium and Caesium chlorides, RbCl and CsCl.—These chlorides resemble those of sodium and potassium, but they have the remarkable property, possessed also by the bromide and iodide of these two elements, of forming additive compounds with the halogens, such as $CsICl_2$ and CsIClBr. Caesium dichloriodide, $CsICl_2$, is an orange salt obtained by treating caesium chloride solutions with iodine and chlorine. On heating, it decomposes into caesium chloride and iodine monochloride, which appears to indicate that it is a double salt of these substances with a formula CsCl.ICl, but it is now proved that it contains a complex anion, ICl_2', analogous to I_3' (see pp. 200 and 757).

Bromides.—These are white crystalline compounds of the general formula MBr, and can be prepared by the direct union of the elements. It is, however, more usual to dissolve bromine in a solution of the hydroxide, to evaporate to dryness, and then to heat strongly, sometimes with the addition of charcoal. The changes which take place with caustic potash are:

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O,$$
$$2KBrO_3 = 2KBr + 3O_2 \uparrow, \quad \text{or} \quad KBrO_3 + 3C = KBr + 3CO \uparrow.$$
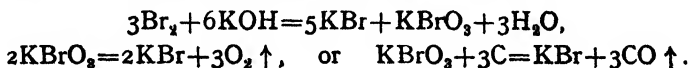
The residue is then once more evaporated with hydrobromic acid to convert any unchanged caustic alkali to bromide.

Potassium bromide is used as a soporific in medicine and in fairly large quantities in the preparation of silver bromide for photographic purposes.

Iodides.—These salts resemble the bromides, and can be prepared by a similar method, but the potassium iodide of commerce is made by neutralizing hydrogen iodide with potassium carbonate. The hydrogen iodide is prepared by the hydrolysis of a solution of ferrous iodide, obtained by shaking up iodine with iron filings and water. The solution is neutralized with potassium carbonate, filtered from ferrous hydroxide and concentrated until the potassium iodide crystallizes out. The chemical changes in this process are:

$$Fe + 2I = Fe^{\cdot\cdot} + 2I'.$$
$$Fe^{\cdot\cdot} + CO_3'' + H_2O = Fe(OH)_2 \downarrow + CO_2 \uparrow.$$
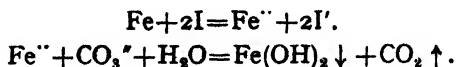
Potassium iodide prepared by this process sometimes contains carbonate as an impurity.

All the alkali-metal iodides are extremely soluble. Even at 0° they all dissolve in less than their own weight of water, and they are also fairly soluble in some organic solvents, lithium iodide usually having the greatest solubility. Potassium iodide is much used in analysis. The yellow colour of solutions which have been

*D

left open to the air is due to the liberation of traces of iodine by oxygen and carbon dioxide:

$$CO_2+H_2O \rightarrow H_2CO_3 \rightleftharpoons H^{\cdot}+HCO_3'. \qquad 4I'+O_2+4H^{\cdot}=2I_2+2H_2O.$$
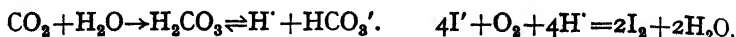
Fluorides.—The fluorides of the alkali-metals are prepared by treating the hydroxide or carbonate with hydrofluoric acid. Since hydrofluoric acid is not a very strong acid, solutions of fluorides have an alkaline reaction and contain the free acid; they therefore etch glass. Lithium fluoride is nearly insoluble in water and sodium fluoride is sparingly soluble. The addition of hydrogen fluoride to the solutions much increases the solubility; this is because acid salts such as $NaHF_2$ (' Fremy's salts ') are formed which are more soluble than the normal salts. The acid fluorides ionize in solution into $M^{\cdot}$ and HF_2' (for the structure of HF_2' see p. 367). On heating they decompose into the normal salt and hydrogen fluoride:

$$KHF_2=KF+HF \uparrow .$$

Fluorine was first obtained by the electrolysis of potassium hydrogen fluoride dissolved in anhydrous liquid hydrogen fluoride (p. 268).

Potassium fluosilicate (or *silicofluoride*), K_2SiF_6, is made from fluosilicic acid, H_2SiF_6, and caustic potash, and is used in estimating potassium, as it is only very slightly soluble in water.

Chlorates.—Potassium chlorate is prepared by the electrolysis of a warm, concentrated, and faintly acidified solution of potassium chloride, without a diaphragm. The total effect of the process is:

$$Cl'+3H_2O=ClO_3'+3H_2,$$
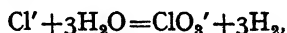
but this result is achieved by distinct stages, only the first of which is electrochemical, as explained on p. 740. To obtain the maximum yield of chlorate from the quantity of electricity passed, wasteful release of gaseous oxygen at the anode must be avoided, and this electrode must be of platinum, which has a high oxygen over-voltage. Reduction at the cathode must also be prevented, by the presence in the electrolyte of small amounts of dissolved chromate or dichromate, which upon initial reduction form a protective film on the cathode.

In another process chlorine is passed into hot lime:

$$3Cl_2+6OH'=5Cl'+ClO_3'+3H_2O,$$
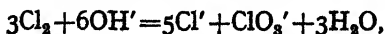
as above, and potassium chlorate is precipitated by adding excess of potassium chloride and cooling the solution with refrigerators. Since the solubility of potassium chlorate increases very rapidly with the temperature, the salt can without difficulty be purified by recrystallization; for this reason it is more often used than sodium chlorate. It is used in the dye industry as an oxidizing

agent, in the manufacture of matches and explosives, and as a disinfectant. In the laboratory it is the commonest source of oxygen gas. On heating, it first decomposes into potassium perchlorate, which then liberates all its oxygen:

$$4KClO_3 = 3KClO_4 + KCl \quad \text{and} \quad KClO_4 = KCl + 2O_2 \uparrow.$$
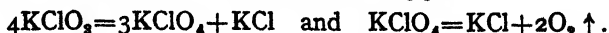
All the alkali-metal chlorates are soluble in water. Lithium chlorate is among the most soluble of all known salts: the solution saturated at room temperature has a density of 1·8 and contains about seventy-five parts of the salt to twenty-five of water.

Perchlorates.—The perchlorates, such as sodium perchlorate, $NaClO_4$, are obtained by electrolysing chlorate solutions at normal temperature. Potassium perchlorate is used in explosives, and is remarkable as being one of the few potassium salts nearly insoluble in cold water (1·08 gm. per 100 gm. water at 10°). Potassium can be separated in this way from sodium: to decrease the solubility alcohol is added to the solution, which must be kept cold, as the salt is very soluble in hot water. Lithium perchlorate was used by RICHARDS and WILLARD in the determination of the atomic weights of lithium and chlorine from the reaction:

$$LiCl + HClO_4 = LiClO_4 + HCl \uparrow.$$

Bromates.—The bromates of the alkali-metals are all soluble in water. The method of preparation from halogen and caustic alkali is similar to that of the iodates. On heating they liberate oxygen more easily than the chlorates:

$$2KBrO_3 = 2KBr + 3O_2 \uparrow.$$

Iodates.—Sodium iodate, $NaIO_3$, accompanies sodium nitrate in South American caliche to the extent of about 0·3 per cent, and this compound is the source of most of the iodine of commerce. It accumulates in the mother liquors left from the crystallization of the sodium nitrate, and is directly converted to iodine without previous isolation (p. 748). Potassium iodate is obtained by recrystallization from caustic potash to which iodine has been added:

$$6KOH + 3I_2 = KIO_3 + 5KI + 3H_2O.$$

It is a salt which can easily be obtained in a high degree of purity, and is increasingly used in volumetric analysis. The fusion of pure potassium iodate is one of the best methods of preparing potassium iodide free from alkali.

Nitrates.—Sodium nitrate, $NaNO_3$, occurs in immense deposits in desert areas of Chile and Peru, and until recent years was practically the only source of combined nitrogen for chemical manures, with the exception of some ammonium nitrate from the gas-works. The supremacy of the Chile nitrate industry is now seriously

threatened by the development of methods of 'fixing' the nitrogen of the air, i.e. causing it to combine either with hydrogen or oxygen. South American crude sodium nitrate is called caliche or 'Chile saltpetre.'

The caliche is broken up, brought into solution by boiling with water, and recrystallized; the product contains about 95 per cent of sodium nitrate and is shipped in bags. About 80 per cent of the production (which reaches nearly three million tons per annum) is applied directly to the soil as a fertilizer; some three-quarters of the remainder is used for making nitric acid, and most of the residue for making potassium nitrate.

Potassium nitrate is made by boiling mixed saturated solutions of sodium nitrate and potassium chloride. At this temperature sodium chloride is much less soluble than potassium chloride, and is consequently deposited, leaving potassium nitrate in solution:

$$NaNO_3 + KCl \rightleftharpoons NaCl \downarrow + KNO_3.$$
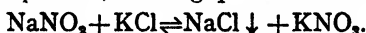
Potassium nitrate is also a product of the bacterial oxidation of decayed animal refuse in the presence of wood-ashes, which contain potassium carbonate, and potassium nitrate produced in this way is extracted from the soil of India and Ceylon. It is used in the manufacture of gunpowder and fireworks, for which the hygroscopic nature of sodium nitrate makes it unsuitable.

On strong heating, the nitrates of the alkali-metals lose oxygen and are converted to nitrites:

$$2NaNO_3 = 2NaNO_2 + O_2 \uparrow.$$

The solids are occasionally used as oxidizing agents.

Nitrites.—Sodium nitrite, $NaNO_2$, is prepared on the large scale by the action of synthetic oxides of nitrogen (p. 411) on caustic soda. It can also be prepared, as above, by heating sodium nitrate. It is used in the diazotization of amines for the manufacture of dyestuffs.

Nitrides.—Lithium is the only alkali-metal to form a nitride by combination with ordinary nitrogen; in this as in other respects it resembles magnesium. The nitride is made by heating lithium in nitrogen:

$$6Li + N_2 = 2Li_3N,$$
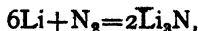
and is decomposed by water to form lithium hydroxide and ammonia:

$$Li_3N + 4H_2O = 3LiOH + NH_4OH.$$

Phosphates.—The phosphates of the alkali-metals, except *lithium phosphate*, Li_3PO_4, are soluble in water, and can be prepared by the action of phosphoric acid on the hydroxide or carbonate. By varying the proportion of acid to base, *trisodium phosphate*,

$Na_3PO_4.12H_2O$, *disodium hydrogen phosphate*, $Na_2HPO_4.12H_2O$, and *sodium dihydrogen phosphate*, $NaH_2PO_4.H_2O$, can all be obtained. The ionization of soluble phosphates and the behaviour of hydrogen phosphates on heating are discussed on p. 629. *Sodium ammonium hydrogen phosphate*, $NaNH_4HPO_4$, once called 'microscomic salt' because it is found in the urine of man, the 'microcosm,' is made from disodium hydrogen phosphate and ammonium chloride, and yields sodium metaphosphate and ammonia on heating:

$$NaNH_4HPO_4 = NaPO_3 + NH_3 \uparrow + H_2O \uparrow.$$

Sulphates.—Sodium sulphate, or salt-cake, Na_2SO_4, was formerly obtained in the now obsolete LEBLANC process for the manufacture of sodium carbonate. The use of sodium sulphate for making glass, in place of the sodium carbonate previously used, gave much-needed support to the Leblanc process, and the first part of this process— the manufacture of sodium sulphate—continues to be worked even now that the Solvay process has driven Leblanc soda from the market. It consists in heating salt with concentrated sulphuric acid in conditions that give the bisulphate, and then heating the bisulphate and unchanged salt on the hearth of a reverberatory furnace, when

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl \uparrow.$$
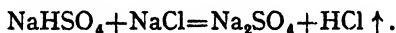
The solubility of sodium sulphate and its hydrates has already been dealt with in Chapter IV (p. 130). The decahydrate, $Na_2SO_4.10H_2O$, is known as GLAUBER'S salt, and is used as a purgative. Potassium sulphate crystallizes anhydrous; it is used as a fertilizer.

When sodium salts are heated with concentrated sulphuric acid, sodium bisulphate, or (better) sodium hydrogen sulphate, is the first product:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl \uparrow.$$
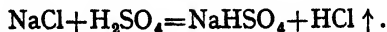
On further heating, some decomposes into the normal sulphate and sulphuric acid:

$$2NaHSO_4 = Na_2SO_4 + H_2SO_4 \uparrow,$$

while some loses water to form sodium pyrosulphate:

$$2NaHSO_4 = Na_2S_2O_7 + H_2O \uparrow.$$

Sodium hydrogen sulphate in solution gives rise to the ions $Na^{\cdot}$, $H^{\cdot}$, SO_4'', and some HSO_4': its solutions have therefore an acid reaction.

Sulphites.—Sodium sulphite, $Na_2SO_3.7H_2O$, is made on the large scale by the action of sulphur dioxide on caustic soda, and under the name of 'antichlor' is used for removing chlorine from substances which have been chlorine-bleached:

$$SO_3'' + Cl_2 + H_2O = SO_4'' + 2HCl.$$

By the continued action of sulphur dioxide, caustic soda is converted to sodium hydrogen sulphite (' sodium bisulphite '), $NaHSO_3$:

$$OH' + SO_2 = HSO_3'.$$
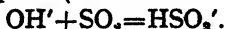
Thiosulphates.—Sodium thiosulphate, $Na_2S_2O_3.5H_2O$, wrongly called ' sodium hyposulphite ' (whence the photographers' name ' hypo '), is made from the still unexhausted waste of the Leblanc process, which contains calcium sulphide, by exposing it to the air, whereby the sulphide is oxidized to thiosulphate. The mass is then extracted with water and sodium carbonate is added to the solution; calcium carbonate is precipitated and sodium thiosulphate remains in solution:

$$CaS_2O_3 + Na_2CO_3 = CaCO_3 \downarrow + Na_2S_2O_3.$$
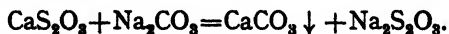
Sodium thiosulphate is a reducing agent used in the volumetric analysis of iodine (p. 691), and, like sodium sulphite, to remove chlorine from bleached goods:

$$S_2O_3'' + 4Cl_2 + 5H_2O = 2SO_4'' + 8Cl' + 10H^{.}.$$
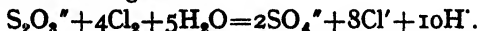
Its use in photography depends on its power of dissolving silver salts insoluble in water: silver forms a complex ion, AgS_2O_3', as follows:

$$AgCl + S_2O_3'' = AgS_2O_3' + Cl'.$$
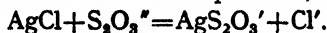
Sulphides.—Sodium sulphide, $Na_2S.9H_2O$, is made on the large scale for use in the dye industry by heating a mixture of sodium sulphate and coal, and extracting the product with water:

$$Na_2SO_4 + 4C = Na_2S + 4CO \uparrow.$$
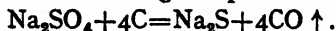
The crystals cannot be dehydrated without decomposition, as hydrogen sulphide is a weak acid, and hydrolysis takes place:

$$Na_2S + 2H_2O = 2NaOH + H_2S \uparrow.$$
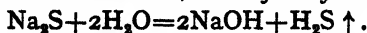
The anhydrous compound can be made by the union of the elements.

The hydrolysis of sulphide solutions proceeds to such an extent that most of the sulphide ions are converted to hydrosulphide ions:

$$S'' + H^{.} \rightleftharpoons HS';$$
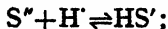
the solutions have consequently a strong alkaline reaction. They can also be prepared by passing hydrogen sulphide into caustic soda:

$$H_2S + OH' = HS' + H_2O.$$
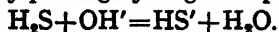
The pure hydrosulphides of the alkali-metals can be made by passing hydrogen sulphide into alcohol in which the alkali-metal has been dissolved:

$$2C_2H_5.OH + 2Na = 2C_2H_5.ONa + H_2 \uparrow.$$
$$H_2S + C_2H_5.ONa = NaHS \downarrow + C_2H_5.OH.$$
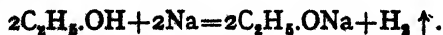
The hydrosulphide is precipitated as a colourless powder.

All sulphide solutions will dissolve sulphur to form polysulphides (p. 677).

Cyanides.—Large quantities of sodium and potassium cyanides are used in electroplating and in the extraction of gold. The cyanide gold-extraction process was introduced by M'ARTHUR and FORREST in 1887, and the demand for cyanide occasioned by it created the sodium industry, since sodium cyanide is usually made from metallic sodium. The two most important processes are:

(i) Sodium ferrocyanide is fused with sodium in covered iron crucibles, and the mass is filtered, while still molten, from the iron produced:

$$Na_4Fe(CN)_6 + 2Na = 6NaCN + Fe.$$

(ii) Wood charcoal and sodium are treated with dry ammonia at 600°, and the product is then heated to 800°. The net result is expressed by the equation:

$$2Na + 2C + 2NH_3 = 2NaCN + 3H_2 \uparrow.$$
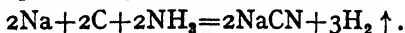
All cyanides are highly poisonous. Hydrogen cyanide is a weak acid, and all cyanide solutions are hydrolysed and have an alkaline reaction; the moist salts smell of hydrogen cyanide. The killing-bottles used by butterfly collectors contain solid potassium cyanide, and the hydrogen cyanide vapour produced by the moisture of the air inside the bottle is enough to kill any captives.

In the laboratory, sodium cyanide is largely used in the production of complex ions with various metals, such as copper, gold, or nickel. Its industrial uses are also based on this property. It is also used as a reducing agent, as the change from cyanide to cyanate takes place easily:

$$CN' + O = OCN'.$$
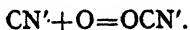
Thiocyanates.—These compounds are made by heating the alkali-metal cyanide with sulphur, e.g.:

$$KCN + S = KSCN.$$

In commerce, thiocyanates are all made from ammonium thiocyanate, which is a by-product of coal-gas manufacture. The alkali-metal thiocyanates are colourless compounds soluble in water; in the laboratory they are used in volumetric analysis.

Other compounds of sodium and potassium are described in later chapters: see the Index.

Detection and Analysis.—The alkali-metals are detected by the colours which their salts—preferably the chlorides—give to the non-luminous flame of the Bunsen burner: *lithium*, red; *sodium*, yellow; *potassium*, violet; *rubidium*, red; *caesium*, blue. The deduction must be confirmed by negative tests for other metals.

The complete separation of the alkali-metals is a matter of great difficulty, on account of their very similar properties and the

scarcity of insoluble salts. *Lithium* can be separated from the others by the solubility of its chloride in organic solvents or the insolubility of the fluoride, carbonate, or phosphate in water. *Potassium* can best be freed from sodium by precipitating it as the fluosilicate or the chloroplatinate, K_2PtCl_6, or by recrystallizing the perchlorate. *Rubidium* and *caesium* are separated from the other alkali-metals and from each other by the silicomolybdate process already described.

The alkali-metals can be weighed as sulphates, but they are more often analysed volumetrically in solutions of their chlorides or carbonates.

SUBGROUP B

COPPER, SILVER, GOLD

The table shows some fundamental physical properties:

	Cu	*Ag*	*Au*
Atomic Number	29	47	79
Atomic Weight	63·54	107·880	197·0
Density of Metal	8·95	10·5	19·3
Atomic Volume	7·1	10·3	10·2
Melting-point	1084°	962°	1064°
Standard Potential (volts)	+0·52 (Cu→Cu·) +0·34 (Cu→Cu··)	+0·80	+1·68 (Au·►Au·)

Copper, silver, and gold are noble metals, eminently malleable and ductile, with high melting-points, and resemble the alkali-metals only in their power of forming salts in which they are univalent. In most other respects they are widely different. They are the best three conductors of electricity, and on account of their permanence are also very widely used in coinage and in electroplating.

The principal valencies are:

Copper: one (unstable), and two (stable).
Silver: one, and two (unstable).
Gold: one, and three (stable only in complexes).

The univalent ions of all these elements are probably colourless; the hydrated cupric ion is blue, and the auric ion scarcely has any independent existence. In its bivalent compounds copper bears some resemblance to its neighbours on either side—nickel and zinc—particularly in its tendency to form complexes, a tendency that decreases in the order cobalt, nickel, copper, zinc.

Copper, silver, and gold all form stable complex ions with ammonia cyanides, and chlorides, though the silver chloride

complex is a good deal less stable than the others. The mono-chloride, monobromide, and monoiodide of copper, silver, and gold are all insoluble in water.

Copper

Cu=63·54. *Atomic Number*, 29

History.—The extraction of copper from its ores was one of the principal triumphs of early civilization. So far as our information goes, this important metallurgical operation was first carried out in Egypt, for the oldest known copper objects (needles and rivet-like pins) were discovered in pre-dynastic tombs in that country, dating from the fifth millennium before Christ. By the time of the New Empire (3000–2550 B.C.) the extraction of copper had become a regular industry, and a few centuries later an Egyptian poet wrote thus of a coppersmith:

> *I saw the smith at his work,*
> *Standing before the vent of his oven.*
> *His fingers were like crocodile-skin.*
> *He stank worse than fish-roe.*

In Sumer and in Asia Minor, knowledge of the simple metallurgy of copper was widespread four thousand years before the Christian era, while copper weapons and toilet articles belonging to the Early Minoan Age (3000–2000 B.C.) have been excavated at the palace of Knossos, in Crete.

Greeks and Romans of the classical age obtained copper largely from the island of Cyprus, whence the name *aes Cyprium,* or ' brass of Cyprus,' modified later into simple *cuprum.* Bronze was probably a later discovery than copper, and was doubtless accidentally produced by the unobserved presence of tin ore in the copper ore. When, however, its composition was elucidated, it was prepared deliberately and was usually preferred to copper on account of its greater hardness and greater resistance to corrosion. Finally it so far displaced pure copper as to give its name to the Bronze Age of civilization.

Occurrence.—In small quantities, copper is almost universally distributed in nature; thus it exists in traces in most soils and foodstuffs, in human blood, and even in seaweed. Native copper occurs in many districts, particularly near Lake Superior, where boulders weighing over four hundred tons have been discovered. The principal ores of copper are: *cuprite* or ' red copper ore,' Cu_2O; *chalcopyrite* or *copper pyrites,* $CuFeS_2$; *copper glance* or *chalcocite,* Cu_2S; *atacamite,* a basic chloride, $CuCl_2.3Cu(OH)_2$; *malachite,* a basic carbonate, $Cu(OH)_2.CuCO_3$; *azurite,* a different basic carbonate, $Cu(OH)_2.2CuCO_3$; and *chrysocolla,* the silicate,

$CuSiO_3.2H_2O$. The chief copper-producing regions are: United States, Chile, Japan, Mexico, Rhodesia, Canada, Belgian Congo, Peru, Spain, Portugal, Germany.

Extraction.—A. Oxide and carbonate ores are mixed with a flux and powdered coke and reduced in a reverberatory furnace:

$$Cu_2O+C=2Cu+CO.$$
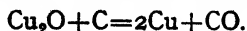
B. By far the greater portion of the metal is, however, extracted from sulphuretted ores, and the treatment is considerably more complicated. Typical procedure is as follows:

(1) The ore is first crushed and then concentrated by differential oil flotation, which eliminates the silica and much of the iron, and leaves a 'concentrate' rich in copper. This method has largely replaced the older concentration by levigation.

(2) The concentrates are then roasted, to remove arsenic and antimony, which are almost always present in the sulphuretted ores. A good deal of the sulphur is removed at the same time.

(3) The roasted ore is next smelted in a furnace, forming a mixture of cuprous sulphide and ferrous sulphide:

$$2CuFeS_2+O_2=Cu_2S+2FeS+SO_2.$$

This mixture is known as 'copper-matte or 'coarse-metal.'

(4) The matte is again smelted, this time with coke and sand (or some other siliceous flux), in a reverberatory furnace, when the silica carries off the iron as a fusible slag of iron silicate. The impure cuprous sulphide that remains as a fused mass beneath the slag is known as 'blue-metal,' 'pimple-metal,' or 'fine-metal,' according to the amount of iron left in it. 'Blue-metal' and 'pimple-metal are subjected to a further smelting, to bring them up to the purity of 'fine-metal' (about 75 per cent Cu).

(5) The 'fine-metal' is heated on the hearth of a reverberatory furnace with free access of air, or in a PIERCE and SMITH basic converter lined with magnesite, through which hot air can be blown. Part of the cuprous sulphide is converted into cuprous oxide, which then reacts with the remainder of the sulphide to form copper and sulphur dioxide:

$$2Cu_2S+3O_2=2\overline{Cu_2O}+2SO_2.$$
$$2Cu_2O+Cu_2S=6Cu+SO_2.$$
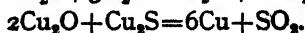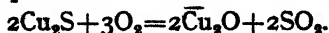
As the mass of copper cools it gives up the sulphur dioxide that was dissolved (or contained) in it; the formation of these bubbles of gas in the copper makes the latter appear to be covered with blisters and it is therefore called 'blister-copper.' It contains about 95–97 per cent Cu.

(6) The blister-copper still contains some 3 to 5 per cent of sulphur,

iron, arsenic, antimony, lead, and other impurities, as well as a little silver and gold—which are often present in sufficient quantity to be worth extracting (see next paragraph). It is run off from the hearth or converter while still molten, and is cast into blocks to serve as anodes for the electrolytic refining process. If the copper is not to be refined, it is melted in a furnace, and stirred up with iron stirrers while a blast of hot air is blown over the surface. In this way, most of the impurities are converted into a slag, which rises to the top and may be skimmed off. To reconvert into copper the cuprous oxide formed in the process (up to 6 per cent), the molten metal is again stirred, this time with poles of green wood ('poling'). 'Poling' is a tricky operation and calls for considerable experience and skill, since if it is continued too long the copper absorbs gases and becomes porous and brittle, while if it is not continued long enough the impurities are not sufficiently removed. Properly 'poled' copper may be used for conversion into tubes, etc., but as formerly produced was not pure enough for electrical work. The product of a new process for the treatment of Rhodesian copper can however compete with electrolytically refined metal.

(7) *Electrolytic Refining.*—The blocks of blister-copper are made anodes in electrolytic cells containing an electrolyte of copper sulphate solution acidified with about 12–15 per cent of sulphuric acid. The cathodes are thin sheets of pure copper, and the cell is maintained at a temperature of approximately 50°; the electrolyte is kept in constant but steady motion, to ensure uniformity of concentration. The theory of the process is discussed on p. 266.

C. The so-called 'hydrometallurgical process' is widely used for extracting copper from low-grade ores, of which vast supplies are available in Spain and other countries. The crushed ore is piled into enormous heaps—running into millions of tons—and is allowed to weather in the presence of water; if the rainfall is insufficient, water is added artificially. After a period of some twelve months, the copper will have become converted into copper sulphate, which remains in solution. The solution is run off into concrete pans and the copper is precipitated by addition of scrap iron. The crude copper so obtained is refined as in method B above.

Note.—The almost complete elimination of impurities from copper is exceedingly important if it is to be used for electrical purposes, since the electrical conductivity is much reduced by traces of foreign substances; thus 0·02 per cent of phosphorus reduces it by 30 per cent. As a matter of fact, the best copper manufactured to-day is so pure that its conductivity is over 100 per cent!—a paradox to be explained by the fact that, at the time the standard

was made, the purest copper obtainable was distinctly less pure than the best specimens now on the market.

Uses and Alloys.—Copper is used in very large quantities in the electrical industry, in coinage, in electroplating, in the manufacture of kettles, pans, and other domestic appliances, and in the manufacture of a wide series of important alloys.

Alloy	Approximate Composition (per cent by weight)
Bell-metal	80 Cu, 20 Sn
Brass	70–80 Cu, 30–20 Zn
Bronze	80–90 Cu, 20–10 Sn
Delta metal	55–60 Cu, 41–38 Zn, 4–2 Fe
German silver	60 Cu, 20 Ni, 20 Zn
Monel metal	27 Cu, 68 Ni, 2–3 Fe; Mn, etc., traces
Phosphor-bronze	99·5 Bronze; 0·5 P
Constantan	60 Cu, 40 Ni
Manganin	81 Cu, 17 Mn, 2 Ni
Aluminium bronze	88 Cu, 8 Al, 4 Mn and Fe
Former British 'silver' coinage	40 Cu, 50 Ag, 5 Ni, 5 Zn

Properties.—Copper is a rosy-pink metal, very malleable and ductile. Its technical importance is due to its high electrical conductivity, in which it is only slightly surpassed by silver; to the ease with which it can be manipulated, and to its resistance to corrosion, particularly when suitably alloyed with other metals. Freezing-point measurements on copper amalgams show the copper contained in them to be monatomic. The vapour is green and probably monatomic.

Copper is stable in dry air at ordinary temperatures, but in moist air it is slowly converted to verdigris, a basic carbonate, whose green colour is so familiar on bronze monuments and on copper roofs. For reasons which will be explained, copper dissolves slightly in water containing traces of ammonium salts or chlorides, and can often be detected in water distilled in a copper still; it is on account of this solubility that ships are usually sheathed not with pure copper but with brass.

Copper will not liberate hydrogen from acids in normal circumstances, and will dissolve only in oxidizing acids and those in which it can form complex ions. It reacts vigorously with nitric acid, dilute or concentrated, to form nitric oxide and nitrogen peroxide:

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO \uparrow$$
$$Cu+4HNO_3=Cu(NO_3)_2+2H_2O+2NO_2 \uparrow,$$
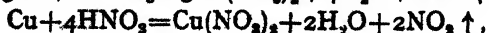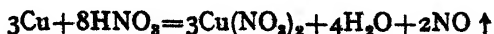
and with hot concentrated sulphuric acid (the dilute acid has no

action) to form sulphur dioxide and a mixture of copper sulphate and copper sulphides. The black colour of the liquid is due to the presence of cuprous sulphide. Copper will also dissolve very slowly in hot concentrated hydrochloric acid containing dissolved air; chloric acid, on the other hand, dissolves it with rapidity. It will also dissolve in aqueous ammonia in a current of air.

THE EQUILIBRIUM BETWEEN COPPER AND COPPER IONS.—Copper is one of the noble metals, and is slowly deposited from solutions containing cupric ions when hydrogen is bubbled through them; for this reason it will not dissolve in acid solutions unless the anion is an oxidizing agent. The standard electrode potentials of the changes $Cu \rightarrow Cu^{..}$ and $Cu \rightarrow Cu^{.}$ are, respectively, $+0.34$ and $+0.52$ volts; while the change $Cu^{..} \rightarrow Cu^{.}$ has a standard potential of -0.16 volts (see p. 259). The affinity of the change from cupric to cuprous ions is thus negative unless the cuprous ion concentration is exceedingly small. Consequently the reversible change $Cu^{.} \rightarrow Cu^{..}$ +electron usually goes to the right, but if the cuprous ion concentration is very small it will move to the left. The nature of the anion is the controlling factor; in the presence of reducing agents cupric salt will be unstable if any anion is present which forms (1) an insoluble cuprous salt or (2) a very stable complex cuprous ion, since in either case the cuprous ion concentration will be reduced to a very low figure. Cuprous salts can therefore only exist in contact with water if they are either insoluble or combined in a complex, and this is amply borne out by experience. Moreover, the affinity of the change $Cu^{..} + Cu \rightarrow 2Cu^{.}$ is negative at ordinary concentrations, so that cuprous salts can be made from cupric solutions and metallic copper only if the cuprous ion concentration is reduced by insolubility or complex formation. These considerations indicate that it is easier to oxidize copper to the cupric state than to the cuprous state in aqueous conditions.

Somewhat similar considerations apply to the univalent salts of both gold and silver. The more easily the anion is discharged, the greater will be the tendency for the metal ion to be deposited as metal. The potential values given on p. 254 show that the reaction $Ag + I^{-} = Ag + I$ tends to move to the right, i.e. silver ion spontaneously oxidizes iodide ion. Thus silver iodide is only saved from decomposition by its extreme insolubility in water. In this connection it is of interest to note that silver iodide below 146° possesses a covalent, non-ionic crystal structure similar to that of the cuprous halides. Above 146° the crystal has marked electrolytic conductivity, the current carriers being exclusively silver ions. The electrode potential of gold is much greater than that of silver, and aurous iodide is decomposed by warm water into gold and iodine.

The insolubility of the monochlorides, bromides, and iodides of copper, silver, and gold is therefore highly significant; in more concentrated solutions these compounds could not exist.

COMPLEX COPPER IONS.—Copper is remarkable for the ease with which it forms a number of stable complex ions. In this respect it resembles its neighbours nickel and cobalt, and, to a less degree, zinc. Since the complexes play a very important part in the chemistry of copper solutions, it will be well to consider them together.

Cupric Ion Complexes.—The formula weight of copper sulphate in solution, as determined by freezing-point measurements, is abnormally high, while the transport numbers vary considerably with the concentration. Both these observations indicate the formation of complexes containing copper and sulphate ions combined in proportions at present unknown. Solutions of cupric chloride have been more fully investigated and show a similar type of auto-complex formation. The copper may actually have a negative transport number (p. 202) in concentrated solutions, and the colour of the solution also depends on the concentration— dilute solutions are blue, concentrated solutions green. It is therefore supposed that solutions of cupric chloride contain both undissociated molecules and also complex ions, probably $CuCl_4''$, and that the complex ions or the molecules are yellow, while the simple ions are blue; the green colour of concentrated solutions is then due to the presence of both blue and yellow forms. The continued addition of hydrochloric acid, which increases the chloride ion concentration and hence reduces the proportion of simple cupric ions, should therefore turn the blue solutions green, and finally yellow, as in fact occurs.

There can be little doubt that this simple explanation is incomplete, for the number of molecules of water associated with the various ions almost certainly affects the colour. The effect of hydrogen chloride may be due as much to its power of removing water for its own hydration, and hence increasing the effective concentration of the solution, as to the mass-action effect of its chloride ions. Thus the green and blue colours have been attributed to cupric ions—or even cupric chloride molecules—in different states of hydration. This hypothesis alone is, however, incapable of explaining the existence of negative transport numbers, and it is probable that both complex-formation and hydration come into play to an extent which has not yet been exactly determined. The student should compare this behaviour with the still more striking case of cobalt chloride.

When ammonia is added to a solution containing cupric ions, the precipitate of cupric hydroxide at first produced readily dis-

solves in excess of ammonia with the formation of the familiar splendid deep blue solution. This solution contains $(Cu.4NH_3)^{..}$ ions, as has been shown by distribution measurements of ammonia between cupric solutions and organic solvents, but in the presence of a large excess of ammonia, ions containing a larger proportion of it may be produced. It requires less than four gram-molecules of ammonia to dissolve one gram-molecule of cupric hydroxide, and it has been shown that in the presence of excess of cupric hydroxide some of it is present in colloidal solution. There is also some evidence for the existence of $(Cu.2NH_3)^{..}$ ions under these conditions.

Some of these blue solutions will dissolve cellulose (e.g. cotton or filter-paper), first oxidizing it to oxycellulose—a property that has been made use of in a process for the manufacture of cuprammonium rayon. The cellulose is precipitated by squirting the solution through fine holes into a weakly acid bath, and the thin threads, as they issue from the holes, are twisted together while still in the bath, sixteen or twenty-four at a time, to make a ' silk ' thread.

Cupric ions also form complexes with numerous hydroxyl-containing organic substances. Thus a cupric solution will give no precipitate with caustic soda containing a tartrate (sodium potassium tartrate, which has a neutral reaction, is commonly used), the solution merely becoming deep blue. The solution thus prepared is called FEHLING's solution, used as a test for organic reducing agents and in the estimation of reducing sugars. Cuprous ions do not form these organic complexes, so that if Fehling's solution is reduced, cuprous oxide is produced as a red precipitate, but the cupric ion must be held in solution as a complex or it would itself be precipitated by the alkali. The complex ion has a double negative charge and is probably ' chelate ' (p. 350) with the structure:

$$\left[\begin{array}{c} O^- \!-\! CO \ OC \!-\! O \quad\quad OH\!-\!CH\!-\!HCOH \\[4pt] \underset{OHCH-CH-OH}{\big|\quad\quad\big|}\overset{\nwarrow\!Cu\!\nearrow}{\big\backslash\,\big/}\underset{O\!-\!\!-\!CO\ OC\!-\!O^-}{\big|\quad\quad\big|} \end{array}\right]^{-\,.}$$
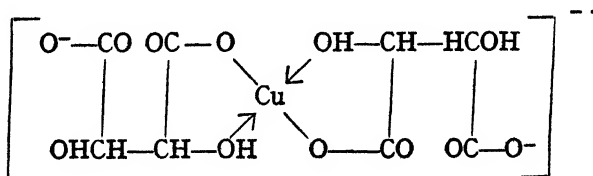
Cuprous Ion Complexes.—The scarcely soluble salt cuprous chloride, CuCl, dissolves very much better in chloride solutions than in water, and solubility measurements show that the formulae of the complexes formed are $CuCl_2'$ and $CuCl_3''$. Cuprous chloride

is usually dissolved either in hydrochloric acid or in ammonia, with which the cuprous ions form a complex. The most important complex cuprous ion is perhaps the cuprocyanide, $Cu(CN)_3''$, which is remarkable for its extreme stability, the equilibrium-constant $\dfrac{[Cu^{\cdot}]\,[CN']^3}{[Cu(CN)_3'']}$ being about 5×10^{-28}. If a cyanide is added to a solution containing cupric ions cyanogen is evolved and cuprous cyanide precipitated, unless there is a sufficient excess of cyanide to dissolve it:

$$2Cu^{\cdot\cdot}+4CN'=C_2N_2 \uparrow +2CuCN \downarrow . \qquad CuCN+2CN'=Cu(CN)_3''.$$
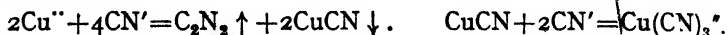
By the addition of cyanides cupric ions can without difficulty be removed from their ammonia complexes.

The extremely low concentration of copper ions in equilibrium with cyanides makes it possible to dissolve the metal in hydrogen cyanide solutions; if they are hot, hydrogen is briskly evolved:

$$2Cu+2H^{\cdot} \rightarrow 2Cu^{\cdot}+H_2 \uparrow \text{ followed by } Cu^{\cdot}+3CN' \rightarrow Cu(CN)_3''.$$

The remarkable nature of this experiment will be appreciated when it is remembered that copper is a noble metal which will not liberate hydrogen from strong acids, and that the hydrogen ion concentration of hydrogen cyanide solutions is very small, on account of the weakness of hydrogen cyanide (dissociation-constant 7×10^{-10}).   In order to give a positive affinity to the change $2Cu+2H^{\cdot} \rightarrow 2Cu^{\cdot}+H_2$, the concentration of cuprous ion must be reduced to an exceedingly low figure, and this can be done by adding cyanides in considerable excess.   For the same reason copper will deposit zinc from cyanide solutions, and if a large excess of cyanide is added to the electrolyte of a DANIELL cell the direction of the E.M.F. is reversed.

In spite of its very low solubility, cuprous sulphide cannot be precipitated from copper solutions containing excess of cyanide. This fact is used in the separation of copper and cadmium, for cadmium sulphide can be quantitatively precipitated from such solutions with ammonia and ammonium sulphide.

Electroplating with copper is usually carried out in a bath containing the cyanide complex, with the object, as explained on p. 268, of reducing the concentration of the metal ion.

OXIDES.—The two most important oxides of copper are cuprous oxide, Cu_2O, and cupric oxide, CuO.

Cuprous oxide, Cu_2O, is obtained from Fehling's solution (p. 461) by reducing it with grape-sugar in the manner already described. It can be obtained pure by carefully heating dry cupric oxide in a current of dry sulphur dioxide:

$$3CuO+SO_2=CuSO_4+Cu_2O.$$
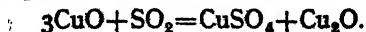
The copper sulphate is extracted with water, leaving pure cuprous

oxide. If the sulphate is heated excessively it loses sulphur trioxide and the cuprous oxide will be contaminated with cupric oxide.

Cuprous oxide is a red powder insoluble in water. It dissolves in acids to form cuprous salts, but these are stable only if they form complex ions with the anion of the acid. Otherwise copper is deposited (it may react with the acid, if the acid is an oxidizing agent) and cupric ions are formed. Thus, with hydrochloric acid, cuprous chloride is produced:

$$Cu_2O + 2H^{\cdot} = 2Cu^{\cdot} + H_2O \quad \text{and} \quad Cu^{\cdot} + 2Cl' = CuCl_2' \quad \text{(also } CuCl_3''\text{)},$$

but with sulphuric acid, cupric sulphate and copper are formed:

$$Cu_2O + 2H^{\cdot} = Cu^{\cdot\cdot} + Cu \downarrow + H_2O,$$
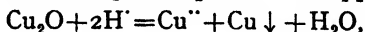
and with nitric acid, cupric nitrate is obtained, but the copper is oxidized by the acid with the liberation of nitric oxide.

Cupric oxide, CuO, is made by heating copper in air, or more conveniently by heating cupric nitrate:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 \uparrow + O_2 \uparrow.$$
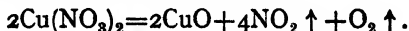
(This is the effective equation. The reaction is actually more complex.) It is a black hygroscopic substance which dissolves in acids forming cupric salts. If strongly heated it gives up some of its oxygen and is converted to cuprous oxide, and is much used in organic analysis for oxidizing the carbon and hydrogen of organic compounds to carbon dioxide and water. It can easily be reduced to the metal by heating in hydrogen.

Copper peroxide, CuO_2, associated with varying amounts of water, can be made by treating solutions of cupric salts with hydrogen peroxide:

$$Cu^{\cdot\cdot} + H_2O_2 = CuO_2 \downarrow + 2H^{\cdot}.$$
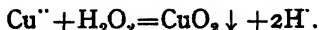
It is insoluble in water, and is a strong oxidizing agent.

HYDROXIDES.—**Cupric hydroxide,** $Cu(OH)_2$, is precipitated, mixed with basic salts, as a blue gelatinous substance when a caustic alkali is added to a solution containing cupric ions. If the solution is boiled the precipitate turns black, and has then the composition $4CuO.H_2O$.

CUPROUS SALTS.—The conditions in which cuprous salts are stable have already been discussed.

It was formerly suggested that copper is bivalent in the cuprous salts, and that the cuprous ion is a complex produced by the union of a cupric ion with a copper atom (compare the mercurous salts, p. 509):

$$Cu^{\cdot\cdot} + Cu \rightleftharpoons (Cu_2)^{\cdot\cdot}.$$
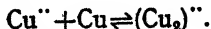
The evidence on this point is decisive, and there appears to be

no doubt that true cuprous ions, $Cu^{\cdot}$, do exist in solution. The chief evidence for the double ion theory was as follows:

   (i) The vapour density of cuprous chloride shows it to exist in the form of double molecules, Cu_2Cl_2, even at 1600°. Cuprous iodide, however, exists in single molecules at 1000°.

   (ii) In some organic solvents the molecular weight of cuprous compounds has been shown by freezing-point measurements to be double; in others, however, it is single.

   (iii) The analogy with mercury, which is certainly bivalent in the mercurous compounds.

On the other hand,

   (i) if copper forms no univalent compounds it is the only element of Group I not to do so;

   (ii) the existence of even one well-authenticated instance of single molecules in organic solvents proves that univalent copper can exist, and there are several such instances;

   (iii) it has been shown from a study of the equilibrium between $Cu^{\cdot}$, $Cu^{\cdot\cdot}$, and metallic copper that the expression $(Cu^{\cdot\cdot})/(Cu^{\cdot})^2$ is nearly constant. This is to be expected if the equilibrium is $2Cu^{\cdot} \rightleftharpoons Cu + Cu^{\cdot\cdot}$, but cannot be reconciled with $(Cu_2^{\cdot\cdot}) \rightleftharpoons Cu + Cu^{\cdot\cdot}$ (cf. p. 510).

The crystal structure of the cuprous halides resembles that of zinc sulphide, and is therefore non-ionic.

The salts with the anions of weak acids are all insoluble in water. The remaining salts are decomposed by water unless they form complexes.

Cuprous chloride, CuCl, is prepared by boiling a solution of cupric chloride in hydrochloric acid with copper turnings:

$$Cu^{\cdot\cdot} + Cu + 4Cl' = 2CuCl_2' \text{ (and } CuCl_3''),$$
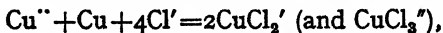
or by reducing the solution with sulphur dioxide:

$$2Cu^{\cdot\cdot} + SO_2 + 2H_2O + 4Cl' = SO_4'' + 4H^{\cdot} + 2CuCl_2' \text{ (and } CuCl_3'').$$
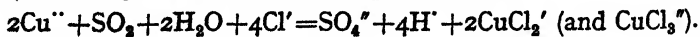
The solution is poured into water from which the air has been removed by boiling; on dilution the hydrochloric acid will no longer take up so much cuprous chloride and the complexes $CuCl_2'$ and $CuCl_3''$ are partially broken down. Cuprous chloride is therefore precipitated.

Cuprous chloride is colourless, insoluble in water but soluble in chloride solutions (usually hydrochloric acid) and in ammonia. In contact with water and air it turns green with the formation of basic cupric chloride, $CuCl_2.Cu(OH)_2$. Ammoniacal solutions of cuprous chloride are used in gas analysis for absorbing carbon

monoxide, which with cuprous chloride forms the colourless compound $CuCl.CO.H_2O$. With acetylene, ammoniacal solutions of cuprous chloride deposit the feebly explosive substance *cuprous acetylide*, Cu_2C_2.

Cuprous chloride is slowly hydrolysed by air-free water with the production of cuprous oxide and hydrochloric acid, particularly if the acid is removed as soon as it is formed (as when the cuprous chloride is washed):

$$2CuCl + H_2O = Cu_2O \downarrow + 2HCl.$$
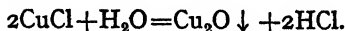
With boiling water, copper and cupric chloride are formed:

$$2CuCl \rightarrow CuCl_2 + Cu \downarrow .$$

Cuprous iodide, CuI, is precipitated when solutions containing *cupric* and iodide ions are mixed, iodine being liberated simultaneously:

$$2Cu\ddot{} + 4I' \rightarrow 2CuI \downarrow + I_2.$$
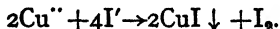
This is one of the examples of the spontaneous production of an insoluble cuprous salt from cupric ions. A similar reaction does not occur with cupric chloride because a higher potential is required to discharge chloride ions as chlorine than iodide ions as iodine. The reaction affords a convenient method for the volumetric analysis of cupric solutions. Excess of an iodide is added and the iodine liberated is titrated against thiosulphate. The reaction is to a slight extent reversible, and to make it go to completion it is best to add to the mixture a little potassium thiocyanate, which forms the very insoluble cuprous thiocyanate with any cuprous ions which may have remained in solution.

Cuprous sulphide, Cu_2S, is formed, together with cupric sulphide, when copper and sulphur are heated together, and can also be obtained by passing hydrogen sulphide through a solution of cuprous chloride in hydrochloric acid. It is insoluble in water.

Cuprous cyanide, CuCN.—The preparation of this substance from solutions containing *cupric* and cyanide ions has already been alluded to.

Cuprous thiocyanate, CuSCN, is an insoluble substance prepared in the same way from cupric solutions and thiocyanates; but in order to accelerate the decomposition of the cupric thiocyanate, a reducing agent such as sulphur dioxide is usually added to the solution.

Cuprous sulphate, Cu_2SO_4, has been made from cuprous oxide and methyl sulphate:

$$Cu_2O + (CH_3)_2SO_4 = Cu_2SO_4 + (CH_3)_2O.$$
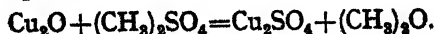
Water must be rigorously excluded during the reaction. The

sulphate is colourless. It is more soluble in water than cuprous chloride, and consequently much more rapidly decomposed by water. An ammoniacal solution of cuprous sulphate can, however, be prepared in which the cuprous ion is combined with ammonia. It rapidly absorbs oxygen if exposed to the air.

Cuprous nitrate, $CuNO_3$, exists only in the form of complex salts, e.g. with acetonitrile, or thiourea.

Cupric Salts.

Cupric chloride, $CuCl_2$, is made by dissolving the oxide, hydroxide, or carbonate in hydrochloric acid and evaporating the solution to crystallization. (The action of chlorine on copper yields a mixture of cuprous and cupric chlorides.) The anhydrous salt can be obtained from the hydrate $CuCl_2.2H_2O$ by warming it gently in a current of dry hydrogen chloride, to prevent hydrolysis. If the temperature rises too high the salt dissociates into cuprous chloride and chlorine:

$$2CuCl_2 = 2CuCl + Cl_2 \uparrow .$$

The anhydrous salt is yellowish-brown and deliquescent; the colour of its aqueous solutions has already been discussed (p. 460). With ammonia cupric chloride forms compounds, $CuCl_2.2NH_3$, $CuCl_2.4NH_3$, $CuCl_2.6NH_3$, in accordance with the rule that complex ions existing in solution usually have their counterpart in the solid state.

Cupric bromide, $CuBr_2$, resembles the chloride.

Cupric iodide has never been prepared. As we have already seen, it could not exist in contact with water.

Cupric carbonate.—The normal carbonate has never been prepared, but a green mineral with the composition $CuCO_3.Cu(OH)_2$ is well known under the name of *malachite*. The precipitates obtained from carbonate solutions and cupric solutions are either basic carbonates or double carbonates such as $CuCO_3.Na_2CO_3$. The basic and double carbonates of copper easily lose carbon dioxide on heating.

Cupric sulphide, CuS, is a brown or black substance precipitated from cupric solutions by hydrogen sulphide or ammonium sulphide. It is very insoluble in water, and will not dissolve in 'yellow ammonium sulphide.' On strong heating, it decomposes into cuprous sulphide and sulphur, but if air is present cupric sulphate is formed.

Cupric sulphate, 'blue vitriol,' $CuSO_4.5H_2O$, is the commonest compound of copper. It is made on the large scale by blowing air through a hot mixture of copper scrap or copper turnings with dilute sulphuric acid:

$$2Cu + 4H^{\cdot} + O_2 = 2Cu^{\cdot\cdot} + 2H_2O.$$

It comes into commerce in large blue crystals.

On heating, it can be successively converted into the *monohydrate* $CuSO_4.H_2O$ and the anhydrous salt $CuSO_4$, a white powder. In the presence of water the white powder becomes blue from formation of the pentahydrate. It is used as a test for water, and also in the dehydration of such substances as the alcohols. On strong heating, it decomposes into cupric oxide and sulphur trioxide:

$$CuSO_4 = CuO + SO_3 \uparrow.$$
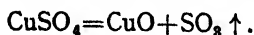
Copper sulphate is very poisonous, especially to the lower forms of plant life, and is used in spraying mixtures to kill the fungus which causes potato disease, and to spray vines. The spraying mixtures usually contain lime ('Bordeaux mixture') or sodium carbonate. Copper sulphate is the usual source of copper for copper-plating.

The anhydrous salt forms a number of compounds with ammonia.

Cupric nitrate, $Cu(NO_3)_2.3H_2O$, is obtained by crystallization from solutions of the oxide, hydroxide, or carbonate in nitric acid. It cannot easily be obtained anhydrous, as on heating the hydrate hydrolysis takes place. The hydrate is a blue deliquescent substance soluble in water.

Cupric ferrocyanide, $Cu_2Fe(CN)_6$, is obtained as a chocolate-coloured gelatinous precipitate when cupric solutions are mixed with ferrocyanide solutions. It has been used in the preparation of semi-permeable membranes for experiments on osmotic pressure (p. 134).

DETECTION AND ESTIMATION OF COPPER.—Cupric solutions are recognized by their colour and by the deep blue solution produced on the addition of ammonia in excess. As was first recorded by Jabir ibn Hayyan, copper compounds give a bluish-green colour to the colourless Bunsen flame. The reaction with potassium iodide solution is also characteristic. Copper can be estimated gravimetrically as the sulphide or oxide, volumetrically with potassium iodide and sodium thiosulphate, or electrically by deposition as metal on a weighed cathode. Colorimetrically, it may be determined by means of sodium diethyl-dithio-carbamate, which produces a brown colour when added to alkaline solutions containing traces of copper.

SILVER

Ag=107·880. *Atomic Number*, 47

History.—Since silver occurs native, and is also easily extracted from its ores, it has been known since very ancient times. During the Old Empire (3000–2500 B.C.) silver was scarce and costly in Egypt, where it was known as 'white gold,' and whither it seems

to have been imported from Asia. Later on, however, it was produced in greater abundance, and its relative value to gold sank to about 1 to 10 or 1 to 13; it will be remembered that in the time of SOLOMON silver was held in little account. The process of cupellation (p. 469) is mentioned by PLINY (first century A.D.), and the 'parting' of gold and silver by means of nitric acid is described by Moslem chemists of the thirteenth century. Among the alchemists, silver was astrologically connected with the moon, and was thus frequently designated *Luna*, and symbolized by the lunar crescent. A relic of this doctrine is to be found in the apothecaries' name for silver nitrate—*lunar caustic.*

Occurrence.—Native silver does not occur in sufficient quantity to be an important source of the metal, though masses weighing up to three-quarters of a ton have occasionally been discovered. The principal ores are *argentite*, Ag_2S; *pyrargyrite*, $3Ag_2S.Sb_2S_3$; *stephanite*, $5Ag_2S.Sb_2S_3$; and *dyscrasite*, Ag_3Sb; but large quantities of silver are also extracted from argentiferous lead and copper ores—thus galena invariably contains silver, the proportion of which may reach some thirteen pounds per ton. The principal silver-producing countries are (in order of output): Mexico, United States, Canada, and Peru.

Extraction.—The chief processes at present in use for the extraction of silver are:

> (i) The cyanide process.
>
> (ii) The desilverization of lead.

A third process, depending upon the formation of an amalgam of silver with mercury, is now nearly, if not quite, obsolete.

Cyanide Process.—The silver ore is first stamped and ground to an impalpable powder. This is then treated for some hours with sodium cyanide solution, air being blown through the liquid, which is contained in a special 'agitating-vat.' The object of the air is to convert the sodium sulphide, formed as a result of the reactions between the silver sulphide and the sodium cyanide, into sodium sulphate. This ensures closer approach to completion of the reaction:

$$Ag_2S + 4CN' \rightleftharpoons 2\overline{Ag}(CN)_2' + S''.$$
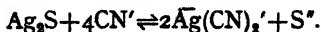
The solution of sodium argentocyanide is then treated with zinc (or aluminium) dust or shavings, when metallic silver is precipitated.

Desilverization of Lead.—In the extraction of lead from galena, the lead carries all the silver with it. To extract the silver, the lead-silver alloy must first be concentrated, an operation usually carried out by either PATTINSON's process or PARKES's process. Pattinson's process depends upon the fact that when argentiferous

lead is allowed to solidify, the crystals that separate first consist of pure lead; removal of this lead results in an alloy richer in silver. Repetition of the operation finally yields an alloy containing about 1 per cent of silver. This is then subjected to *cupellation* (see below).

Parkes's process, now almost exclusively used, is based upon the facts (1) that molten zinc and molten lead are nearly immiscible, and (2) that silver is much more soluble in zinc than in lead (the distribution coefficient at 800° is about 300). Hence, when zinc is added to molten argentiferous lead, most of the silver forms an alloy with the zinc. This alloy floats on the surface of the molten lead, and, on cooling, solidifies before the latter. It is skimmed off, the zinc is removed by distillation from plumbago retorts, and the residual alloy of silver with a little lead is then cupelled. If necessary, the desilverizing process can be carried out two or three times, and the residual lead may then contain as little as 0·0005 per cent of silver.

Poor silver ores are sometimes mixed with lead ores, in order that the metal may be extracted as above.

Cupellation.—The enriched silver-lead alloy resulting from Parkes's process or Pattinson's process is melted in a shallow hearth or ' test ' made of bone-ash (calcium phosphate), or, more usually, cement. A current of air is blown on to the molten metal, when the lead is oxidized to litharge, which is absorbed by the bone-ash:

$$2Pb + O_2 = 2PbO.$$
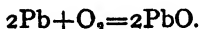
When the lead has all been oxidized away, a bright surface of shining metallic silver suddenly appears, marking the end of the operation.

Refinement of Silver.—The silver obtained by careful cupellation is pure enough for most purposes, though if it contains gold this is removed from it by ' parting ' with nitric acid or sulphuric acid (see p. 473). RICHARDS and WELLS obtained very pure silver by the method described below.

Uses.—Silver is used in coinage and in the manufacture of tableware and ornaments. Since the pure metal is rather soft, it is generally alloyed with copper, of which the old British coinage silver contained 7·5 per cent. Silver crucibles are occasionally used in the laboratory for the fusion of the caustic alkalis, which attack most other metals. During a temporary fall in price, the use of silver for containers of acids and other corrosive liquids extended to industry.

Compounds of silver are used in photography, in making markingink, and in volumetric analysis.

Properties.—Silver is a white metal which will take a high polish

and has been used in making mirrors. Silver vapour is blue, and vapour-density measurements show it to be monatomic.

Silver is a typical noble metal, and as it forms only one series of stable salts its chemistry is simpler than that of either copper or gold. Silver is unaffected by pure air but tarnishes in air containing traces of hydrogen sulphide, always found in towns from the burning of coal; the black substance formed is silver sulphide. Silver egg-spoons rapidly become black for a similar reason—eggs contain combined sulphur. Like copper, silver will dissolve only in acids which oxidize it or form complexes with it. With nitric acid it gives silver nitrate and nitrogen oxides, and with hot concentrated sulphuric acid, sulphur dioxide and the insoluble compound silver sulphate; dilute sulphuric acid has no action. Hydrochloric acid has only a very slight action.

Silver can be made in a state of very great purity. It is precipitated from a solution of pure silver nitrate with an organic reducing agent (sugar), and the product is fused in a boat made of pure quicklime. By this process Richards and Wells were able to prepare a metal for atomic weight determinations with a purity of 99·999 per cent. The fusion must be carried out in hydrogen or in a vacuum, for molten silver absorbs considerable quantities of oxygen, which are given out on cooling; the evolution of gas is called 'spitting,' and leaves marks on the surface of silver which has been melted in air.

Complex Silver Ions.—Silver resembles copper in the formation of stable complexes with ammonia, cyanides, and, to a less degree, chlorides; it also forms complexes with sulphites and thiosulphates (p. 691).

The ammonia complex, which has the formula $(Ag.2NH_3)^{\cdot}$, is used in qualitative analysis in distinguishing between the chloride, bromide, and iodide of silver, for ammonia in ordinary concentrations dissolves the chloride readily, the bromide with difficulty, and the iodide scarcely at all. The action in each case is the same, e.g.:

$$AgCl + 2NH_3 = (Ag.2NH_3)^{\cdot} + Cl',$$
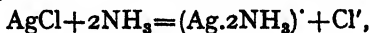
and the difference in behaviour is due to the different solubility products of the three compounds, which are approximately as follows:

$$[Ag^{\cdot}][Cl'] = 2 \times 10^{-10}. \quad [Ag^{\cdot}][Br'] = 4 \times 10^{-13}. \quad [Ag^{\cdot}][I'] = 10^{-16}.$$

The dissociation of the complex ion is controlled by the equation:

$\dfrac{[Ag^{\cdot}][NH_3]^2}{[Ag.2NH_3]} = 7 \times 10^{-8}$, and it can be shown without difficulty

that the observed facts are in agreement with calculation. Since the solubility product of silver sulphide, $[Ag^{\cdot}]^2[S'']$, is about 10^{-50}.

it is obvious that silver sulphide can be precipitated from ammoniacal solutions of any concentration.

The cyanide complex is exceedingly stable, and exists in two forms, $Ag(CN)_2'$ and $Ag(CN)_3''$. The latter is produced in solutions containing a large excess of cyanide, and removes all but a very few silver ions from the solution, as can be seen from the very low value of the dissociation-constant, $\dfrac{[Ag^{\cdot}]\,[CN']^3}{[Ag(CN)_3'']} = 10^{-22}$. Solutions of cyanides will therefore dissolve all the insoluble salts of silver—even silver sulphide if they are sufficiently concentrated—and silver-cleaning powders are sometimes found to contain potassium cyanide, a most undesirable ingredient. Cyanide solutions are used in the wet extraction process for silver, and in silver-plating baths to reduce the concentration of silver ion.

The complex chloride ion, probably $AgCl_2'$ or $AgCl_3''$, is much less stable than those just discussed, but it causes a noticeable solubility of silver chloride in chloride solutions which must be guarded against in analysis.

OXIDES.—**Argentous oxide**, Ag_2O, is precipitated as a brown or black substance when caustic alkalis are added to silver solutions:

$$2Ag^{\cdot} + 2OH' = Ag_2O \downarrow + H_2O.$$

If ammonia is used the oxide easily dissolves in excess of ammonia, and the resulting solution is used as a test for reducing agents, which precipitate silver as a black precipitate, a mirror on the side of the vessel, or a colloidal solution of varying colour:

$$Ag^{\cdot} + electron \rightarrow Ag \downarrow .$$

Silver oxide is easily decomposed by heat into the metal and oxygen. No hydroxide is known. The ammoniacal solution, when oxidized by the air, deposits a black explosive substance called ' fulminating silver,' believed to be silver nitride, Ag_3N.

Argentic oxide, AgO, precipitated from silver solutions by ozone or persulphates, is black, unstable, and a strong oxidizing agent which will convert ammonia to nitrogen.

SILVER SALTS.—All the salts that silver forms with the anions of weak acids are insoluble or only slightly soluble in water (*compare* copper), and so are the halides, except the fluoride, a phenomenon which has already been discussed on p. 459. The sulphate also is only slightly soluble, so the only common soluble salts are the nitrate, chlorate, perchlorate, and fluoride, though with ammonia, or cyanides solutions can easily be obtained containing silver in the form of complex ions. The insolubility of the silver salts of organic acids is often made use of in organic chemistry.

Silver carbonate, Ag_2CO_3, is a pale yellow substance precipitated

Q

when ammoniacal silver solutions are treated with carbon dioxide. It is readily decomposed on heating, first into silver oxide and then into silver.

Silver nitrate, $AgNO_3$, 'lunar caustic,' is the commonest compound of silver, and is made from silver and nitric acid. A solution of silver nitrate is used as marking-ink, since it is reduced to metallic silver (black in the finely-divided form) by organic matter, and the silver precipitated in the fibres of the material cannot be washed out. For the same reason silver nitrate solutions colour the skin black.

SILVER HALIDES, $AgCl$, $AgBr$, AgI, are precipitated as white or pale yellow precipitates when silver solutions are mixed with solutions of the corresponding halide. As already mentioned, they are all insoluble in water, but are soluble in suitable complex-forming reagents. They are often precipitated in the colloidal form but can usually be coagulated by shaking or boiling. They all grow darker on exposure to light, a phenomenon which is used in photography and which, as has been explained on p. 274, is due to the formation of metallic silver. The solid halides all combine with ammonia to form compounds such as $2AgCl.3NH_3$.

Argentous fluoride, AgF, is remarkable as being the only silver halide soluble in water. The bright yellow anhydrous salt and the colourless hydrate, $AgF.2H_2O$, are both extremely deliquescent. Owing to hydrolysis a black precipitate of mixed metal and oxide separates from the hot aqueous solution.

Argentic fluoride, AgF_2, is obtained as a dark-coloured solid by heating silver chloride in fluorine. With water oxygen is released and argentous fluoride formed. The strong magnetic properties reveal the presence of $Ag^{\cdot\cdot}$, which unlike $Ag^{\cdot}$, has an odd number of electrons.

Silver sulphate, Ag_2SO_4, is obtained by precipitating silver solutions with excess of sulphuric acid. It is only slightly soluble in water (about 1 per cent at room temperature).

Silver sulphite, Ag_2SO_3, is insoluble, but readily dissolves in sulphite solutions, forming the complex ion $AgSO_3'$.

Silver sulphide, Ag_2S, is a very insoluble black substance produced when silver solutions are mixed with sulphides. When heated in air, it forms silver and sulphur dioxide:

$$Ag_2S + O_2 = 2Ag + SO_2 \uparrow.$$
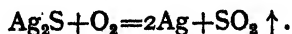
Silver thiocyanate, $AgSCN$, is very insoluble, a fact which is made use of in VOLHARD's titration of silver nitrate against ammonium thiocyanate. The solubility-product, 10^{-12}, is considerably less than that of silver chloride.

DETECTION AND ESTIMATION OF SILVER.—Silver is detected by the precipitate which its solutions give with chlorides, soluble in ammonia but not in dilute nitric acid. It can be estimated gravimetrically as silver chloride, and volumetrically by titration against a chloride, bromide, iodide, or thiocyanate. There is no satisfactory colorimetric method of determining silver.

GOLD

Au = 197·0. *Atomic Number*, 79

History.—Like silver, gold has been known from prehistoric times. The universal esteem in which it has been held for several thousand years is a queer but immeasurably important psychological phenomenon. It has already been mentioned, in the Historical Introduction, that the desire for gold was a deciding factor in the development of chemistry. Alchemical literature is almost entirely a literature of the supposed art of gold-making; and alchemy, of the cruder sort, is still practised—not merely in backward countries, but in the western civilizations. It is worth reflecting that if ever gold is prepared synthetically on a large scale, it will, *ipso facto*, lose its peculiar value: a point which DIOCLETIAN was shrewd enough to perceive, but which rarely entered the consciousness of an alchemist.

Occurrence.—Gold mainly occurs native, though it is frequently present in the ores of other metals to an extent which makes its extraction from them profitable. The native masses vary in size from microscopic grains to lumps weighing as much as 180–90 lb. The principal gold-producing countries (in order of output) are: South Africa, Russia, United States, and Australasia, the first accounting for nearly half the total.

Extraction.—Gold is now extracted from its ores by the wet or cyanide process, which can be applied to ores or residues relatively poor in gold. It was introduced by M'ARTHUR and FORREST in 1887, and it is said that one mine, after putting up a plant costing £2,000, made with it a working profit of £3,000 a month.

In this process the finely-crushed material is thoroughly extracted in the presence of air with a solution of sodium cyanide, in which the gold dissolves to form aurocyanide ions:

$$4Au + 8CN' + O_2 + 2H_2O = 4Au(CN)_2' + 4OH'.$$
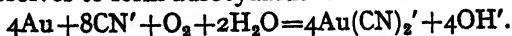
The gold is precipitated from this solution by zinc, and refined either electrolytically or with the help of the volatile compound auric chloride.

Separation of Gold from Silver.—In the extraction of silver, the product frequently consists of a silver-gold alloy with a small

though valuable proportion of the latter element. Separation or 'parting' is effected (a) by digesting with hot concentrated nitric acid, which dissolves the silver and leaves the gold as a brown powder, or (b) by boiling first with sulphuric acid and then with nitric acid, in which case the gold is left as a brown porous mass, and the silver passes into solution as silver sulphate.

Properties.—Gold is a yellow metal which melts at 1064° to a green liquid. It is the most ductile and the most malleable of all metals, and can be beaten out into sheets (called 'gold leaf') as thin as 0·00001 mm., or drawn out into very thin wire. Its high density (19·3) makes it very difficult to counterfeit, as gold which has been alloyed with a less precious metal such as silver has a much lower density; a fact which according to tradition was first applied by Archimedes. Colloidal solutions of gold can be prepared by reducing gold solutions with such reducing agents as phosphorus, hydrazine, or formaldehyde, and are usually brightly coloured. The pigment called 'purple of Cassius' was discovered by CASSIUS in 1685, and is a colloidal solution of gold in stannic oxide, prepared by reducing gold solutions with stannous chloride. It has a fine red or purple colour and is used in colouring glass or porcelain. R. CAMPBELL THOMPSON has adduced evidence suggesting that purple of Cassius was known to the ancient Assyrian glass-makers.

Gold has a standard electrode potential of about 1·7 volts, and is one of the most noble of the metals; it will dissolve only in solutions with which it can form complexes. It can be dissolved by aqua regia, a mixture of nitric and hydrochloric acids in the proportion of about one to three; this mixture evolves chlorine, by which gold is readily attacked, and the metal dissolves to form chlorauric ions, $AuCl_4'$. The solubility of gold in cyanide solutions in the presence of air has already been mentioned.

Gilding is carried out either by electroplating from a gold cyanide bath or by applying gold leaf to the surface of the object. The chief use of gold is, however, in coinage or jewelry. Since pure gold is soft it is for these purposes alloyed either with silver (as in Australian coinage) or with copper (as in the former English coinage): the former alloy is pale yellow, the latter almost orange. The proportion of gold in such alloys is said to be 22 carats, which means that they contain 22 parts of gold by weight in 24; pure gold is 24-carat.

OXIDES AND HYDROXIDES.

Aurous oxide, Au_2O, is obtained by reducing a solution of an aurichloride with sulphur dioxide and adding caustic alkali:

$$AuCl_4' + SO_2 + 2H_2O + OH' = AuOH \downarrow + 4H' + SO_4'' + 4Cl'.$$
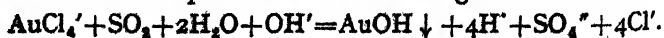
The black aurous hydroxide loses water on gentle heating to form aurous oxide, which is itself easily decomposed at a higher temperature into gold and oxygen.

Auric hydroxide, $AuO.OH$, is precipitated by adding caustic alkali to a solution of auric chloride, $AuCl_3$:

$$AuCl_3 + 3OH' = AuO.OH \downarrow + 3Cl' + H_2O.$$
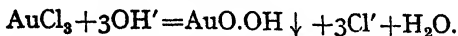
The hydroxide is soluble in excess of caustic alkali, so it is best to carry out the precipitation with the almost insoluble magnesium hydroxide. Any excess of this reagent can be removed from the precipitate by washing it with dilute nitric acid.

Auric hydroxide dissolves in caustic alkalis because it is a weak acid (it is sometimes called auric acid); in such alkaline solutions the gold is in the anion. The hydroxide is decomposed at a moderate temperature into gold, water, and oxygen. With ammonia 'fulminating gold' can be obtained; it resembles the analogous silver compound in its properties.

GOLD COMPOUNDS.—These form two series, the *aurous*, in which gold is univalent, and the *auric*, in which it is tervalent. The auric compounds are covalent and do not give measurable quantities of auric ions in solution (compare the quadrivalency of lead): they are not very stable except in the form of complexes such as the *chloraurates*, $AuCl_4'$. The aurous *halides*, like the cuprous and argentous (the fluoride excepted), are insoluble in water, and for the same reason. Like the mono-halides of copper they are decomposed by boiling water into higher halide and metal; the auric halide may decompose further into gold and halogen. Like the auric compounds, they form fairly stable complexes (such as $AuCl_2'$) with halide ions, and are consequently soluble in halide solutions, and they also form complexes with ammonia.

Gold forms a very stable *aurocyanide* complex, $Au(CN)_2'$, and all compounds of gold will dissolve in cyanide solutions. Gold itself has a much higher standard electrode potential than copper ($+1.7$ volts against 0.52 volts), and unlike copper will not liberate hydrogen from cyanide solutions, but it will dissolve in them if there is air present to oxidize the hydrogen.

AUROUS COMPOUNDS.

Aurous chloride, $AuCl$, is obtained by gently heating auric chloride:

$$AuCl_3 = AuCl + Cl_2 \uparrow.$$

It is insoluble in cold water and decomposed by hot water into auric chloride and gold:

$$3AuCl = 2Au \downarrow + AuCl_3.$$

Like cuprous chloride and silver chloride, aurous chloride is soluble in ammonia, and the solid forms compounds with ammonia gas.

Aurous iodide, AuI, is produced when an iodide solution is added to an aurous *or an auric* solution; in this respect it resembles cuprous iodide:

$$AuCl_3 + 3I' = AuI \downarrow + I_2 + 3Cl'.$$

It is unstable and is easily decomposed into its elements.

Aurous sulphide, Au_2S, is precipitated in somewhat similar fashion by a sulphide from either aurous or auric solutions. It is a black insoluble substance:

$$2AuCl_3 + 3S'' = Au_2S \downarrow + 2S \downarrow + 6Cl'.$$

AURIC COMPOUNDS.

Auric chloride, $AuCl_3$, is prepared by the action of chlorine on gold. It forms a hydrate, $AuCl_3.2H_2O$, and is soluble in water, but it is a covalent compound and its solutions do not contain auric ions—which indeed appear not to exist. The low melting-point (288°) and the volatility support this view, and the electrical conductivity of a freshly prepared solution was found by KOHLRAUSCH to be very small at first, gradually rising with the formation of hydrogen chloride by hydrolysis. Auric chloride is soluble in some organic solvents—another indication of covalency. When heated it decomposes into aurous chloride and chlorine.

It is stable in chloride solutions, in which it forms the anion $AuCl_4'$; from the hydrochloric acid solution *chloroauric acid* has been isolated as the hydrate $HAuCl_4.3H_2O$. This is used in photography, under the name of ' chloride of gold,' for toning prints.

Auric iodide, AuI_3, is less stable than the chloride and is decomposed at a lower temperature into aurous halide and halogen. It is also decomposed by water, but stable solutions of iodo-aurates can be prepared containing the anion AuI_4'.

GROUP II

BERYLLIUM, MAGNESIUM, CALCIUM, STRONTIUM, BARIUM,
[RADIUM], ZINC, CADMIUM, MERCURY

$$\text{Be—Mg}\begin{cases}\text{Ca—Sr—Ba—[Ra]}\\\text{Zn—Cd—Hg}\end{cases}$$
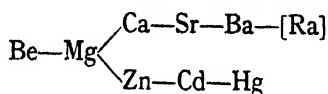
	Typical Elements		Subgroup A (Alkaline earths)				Subgroup B		
	Be	Mg	Ca	Sr	Ba	Ra	Zn	Cd	Hg
Atomic Number	4	12	20	38	56	88	30	48	80
Atomic Weight	9·01	24·32	40·08	87·63	137·36	225·97	65·38	112·41	200·61
Density	1·83	1·74	1·74	2·5	3·8	6·0	6·9	8·6	13·61
Atomic Volume	4·92	14·0	25·0	35·1	36·7	38	9·5	13·0	14·1
Melting-point	1280°	650°	810°	752°	830°	700°	420°	320°	−39°
Boiling-point	2970°	1100°	1440°	1366°	1737°	?	920°	780°	360°
Standard Electrode Potential (volts)	−1·70	−2·34	−2·87	−2·89	−2·90	?	−0·76	−0·40	+0·80 (-ous)

THE chemical properties of radium and its compounds have not been sufficiently thoroughly investigated to receive separate treatment here. In so far as they are known they closely resemble those of barium.

The order of the standard electrode potentials is:

Ba, Sr, Ca, Mg, Be, Zn, Cd, Hg,

that is, from the heaviest element of Subgroup A to the heaviest element of Subgroup B, the typical elements occupying an intermediate position. The subgroups do not resemble each other very closely, but the valency in all the soluble compounds is two: the mercurous compounds are only an apparent exception to this rule, as will be seen when we come to study them. The typical elements resemble sometimes one subgroup and sometimes the other, but, on the whole, magnesium goes with Subgroup A and beryllium with Subgroup B, that is, the dividing line in the series given above is to be drawn between Mg and Be.

1. The action of the metals on water is what would be expected from the electrode potentials, and ranges from barium, which

reacts very vigorously, to mercury, which is readily precipitated by reducing agents from solutions of its salts. The action of air on the metal follows the same order.

2. The same is true of the tendency of the elements to form covalent compounds, though beryllium, with its very small atomic volume, is perhaps more prominent in this direction than its position in the electrochemical series might indicate. The Sub-group A elements, with their very low densities and their high atomic volumes, form predominantly electrovalent compounds, while the Subgroup B elements, with their high densities and low atomic volumes, form partly electrovalent and partly covalent compounds. These covalent compounds have comparatively low melting- and boiling-points and are soluble in organic solvents, while their solutions contain a considerable proportion of unionized molecules. It is instructive to compare the melting-points of the chlorides in the two groups:

Mg	700°	Be	400°
Ca	800°	Zn	290°
Sr	870°	Cd	563°
Ba	960°	Hg	265°
Ra	1000°?		

The chlorides in the right-hand group are all freely soluble in organic solvents, those in the left-hand group are not, except to some extent calcium chloride.

The power of forming covalent organic compounds begins with magnesium and is very marked with mercury.

3. The tendency to form complex ions and auto-complexes increases in the same order: it is unimportant in Subgroup A, though already appreciable in calcium; marked with beryllium; and very prominent with zinc and especially cadmium; while the mercurous ion, a complex, is so stable that it was formerly mistaken for a separate valency type. The same applies to the tendency of the salts to form hydrates—but mercury is an exception to this. The ions of all these elements are colourless.

4. The hydroxides of Subgroup A are soluble or slightly soluble in water: those of the typical elements and Subgroup B are nearly insoluble. Magnesium and Subgroup A hydroxides are strongly basic, while the others are weak bases also possessed of feeble acidic powers, which decrease in the usual way with the atomic number of the metal.

5. The ease with which the hydroxides, peroxides, carbonates, sulphates, and nitrates can be decomposed by heating increases fairly regularly from barium to mercury (but beryllium forms no peroxide).

6. Subgroup A metals share with the alkali-metals the power of

forming hydrides of electrovalent type (formula MH_2) when the metal is heated in hydrogen; the remaining elements of the group form no similar hydrides.

7. The typical and Subgroup A elements form nitrides of formula M_3N_2 on heating in nitrogen; Subgroup B elements do not readily form nitrides.

8. Solubility differences include the following:

The *fluorides* of magnesium and Subgroup A metals are nearly insoluble; the rest soluble.

The *sulphides* of Subgroup B are insoluble; the rest are decomposed by water.

The *sulphates* of Subgroup A are insoluble or slightly soluble; the rest (except the mercury sulphates) very soluble.

It must not be supposed that all the compounds of all the elements in this group have properties that can be arranged in sequence: such is very far from being the case. Beryllium, as is usual with the first element of a group, closely resembles aluminium, the second element of the next, just as magnesium resembles lithium, while both beryllium and mercury are highly individual elements whose compounds show peculiarities which can be subjected only to a limited extent to the generalities of the periodic classification.

BERYLLIUM

Be=9·01. *Atomic Number, 4*

History.—HAÜY, one of the founders of crystallography, noticed that the mineral beryl had the same crystal form as the emerald, and invited the French chemist VAUQUELIN to analyse these substances. The result was the discovery in 1798 of a new element, resembling aluminium in its properties, but with certain characteristics of its own, among them the sweet taste of its salts. The name *glucinum* was therefore given to the newly discovered element, but has now been almost superseded by the name *beryllium*.

Occurrence.—Beryllium is the scarcest element of the second group, excepting only radium, and the least known of all the typical elements. Up to the present time it has been of trifling commercial importance and the principal source has been beryl, an impure beryllium aluminosilicate which occurs in small quantities in various parts of the world, chiefly in the United States. Recently, however, important new deposits of beryllium minerals have been discovered in Manitoba, Canada, as the result of a search stimulated by the invention of light alloys in which the metal advantageously replaces the heavier aluminium, and in the future the production

*Q

of beryllium may be expected to increase. A minor use of beryllium is as a ' window ' in some varieties of X-ray tubes.

Extraction.—Beryllium is now extracted on a commercial scale as follows:

Beryl is mixed with sodium fluosilicate, heated to 650°, and extracted with cold water. The beryllium passes into solution as sodium fluoberyllate, Na_2BeF_4, which can be crystallized. From a solution of this compound caustic alkali precipitates beryllium hydroxide, $Be(OH)_2$, which is dissolved in hydrofluoric acid and evaporated to dryness, leaving $2BeO.BeF_2$, which melts at 750°. This compound is mixed with barium fluoride and electrolysed at 1400° in a graphite crucible which acts as anode. The cathode is a water-cooled iron tube on which rough rods of beryllium form.

Small quantities of pure beryllium may be prepared by the electrolysis of anhydrous beryllium salts dissolved in liquid ammonia.

Properties.—Metallic beryllium resembles magnesium and aluminium, but has a higher melting-point than either. The chemistry of its compounds is dominated by its very low atomic volume, lower than that of any other element, which causes its compounds to be largely covalent, and associates them with those of aluminium, which they otherwise much resemble.

Beryllium is a hard, grey metal with a density (1·83) lower than that of aluminium, though greater than that of magnesium. It has the highest melting-point of any element in the group, and is a good conductor of electricity. Its physical qualities are superior to those of aluminium, but unfortunately it is far less common. It is as stable as aluminium in the air, but if the finely-divided metal is strongly heated it burns with a bright light to form beryllium oxide. Its standard electrode potential certainly lies between those of magnesium and zinc, and it is more resistant than magnesium to the action of water, from which it displaces hydrogen slowly or not at all, owing to the formation of a film of oxide. It is readily soluble in acids, and differs from magnesium in dissolving in solutions of alkalis.

Oxides and Hydroxides.—The only known oxide of beryllium is the monoxide $.BeO$. It can be obtained by heating the carbonate or nitrate or the hydroxide, $Be(OH)_2$.— This latter compound is precipitated from beryllium solutions by caustic alkalis, but dissolves in excess, like aluminium hydroxide, to form compounds called beryllates:

$$Be(OH)_2 + 2OH' \rightleftharpoons BeO_2'' + 2H_2O,$$
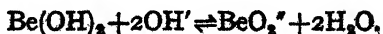
On boiling the solution the reverse change takes place and beryllium hydroxide, unlike aluminium hydroxide, is reprecipitated: this is

used in the separation of the two elements. Solutions of the beryllates, though less stable than those of the aluminates, are more stable than those of the zincates.

The oxide can be purified by heating it in a current of carbonyl chloride at 450° for one or two hours. Iron and aluminium are removed as volatile chlorides. After calcium chloride and any beryllium chloride have been washed out with water, pure beryllium oxide remains. It is a colourless compound with a very high melting-point (2500°?). It dissolves in acids to form the beryllium salts, and in alkalis to form the beryllates. It has the wurtzite structure exactly like ZnO, and utterly different from the rock-salt structure of MgO, CaO, etc.

Nitride.—Like magnesium, beryllium combines with nitrogen when heated in the gas. The product, which has the formula Be_3N_2, can also be prepared by heating the metal in ammonia.

Carbonate.—The normal carbonate is unknown: sodium carbonate precipitates from beryllium solutions a basic carbonate of uncertain composition.

Halides.—Solutions of the halides are prepared in the ordinary way by the action of the acid on the metal, oxide, or carbonate, but evaporation of the solutions always leads to the precipitation of beryllium hydroxide or of a basic salt formed by hydrolysis. The anhydrous salts are therefore prepared by the action of the halogen or hydrogen halide on the metal, or on a heated mixture of the oxide and carbon (compare aluminium).

Fluoride, BeF_2.—This compound can be prepared by heating the complex salt $(NH_4)_2BeF_4$ in the absence of air. It is a glassy hygroscopic substance soluble in water: the fused salt is a non-conductor. The fluoride must be heated to a higher temperature than the other halides before it is fully liquid. The structure of BeF_2 resembles that of quartz (with Be=Si, and F=O).

Chloride, $BeCl_2$.—A white solid melting at 400° and boiling at 520°. The vapour density of this compound was determined as a check on the atomic weight (and valency) of beryllium: it showed the molecule to be $BeCl_2$.

The *bromide* melts at 490° and the *iodide* at 510°. All the halides are soluble in organic solvents, but the fluoride is only slightly soluble.

Sulphide.—The compound BeS is immediately decomposed by water, and attempts to precipitate it from beryllium solutions with ammonium sulphide lead to the evolution of hydrogen sulphide and the precipitation of the hydroxide:

$$BeS + 2H_2O = Be(OH)_2 \downarrow + H_2S \uparrow .$$
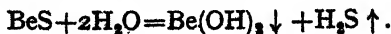
Sulphate.—Solutions of this compound can be obtained by the usual methods, but the anhydrous compound $BeSO_4$ has not been

prepared in a state of purity, as the attempt to remove the 1, 2, 4, or 6 molecules of water of crystallization by heating it leads to partial decomposition; on strong heating the oxide remains.

Nitrate.—The hydrated nitrate can be prepared by the usual methods, and dehydrated by heating with amyl alcohol.

<center>

✳

MAGNESIUM

$Mg = 24 \cdot 32.$ *Atomic Number*, 12

</center>

History.—Magnesium sulphate was discovered in the water of a well at Epsom by NATHANIEL GREW in 1695. HOFFMANN, in 1729, first showed that magnesia (MgO) was to be distinguished from lime (CaO), and BLACK (1755) elucidated the composition of *magnesia alba* (a carbonate of magnesium). The metal was possibly obtained by SAGE in 1777, and was certainly prepared in an impure state by DAVY in 1808. In a state of comparative purity it was first obtained by BUSSY (1829).

Occurrence.—Magnesium is an abundant element. It occurs in *carnallite*, $MgCl_2.KCl.6H_2O$ (p. 445); *magnesite*, $MgCO_3$; *dolomite*, $MgCO_3.CaCO_3$; *kieserite*, $MgSO_4.H_2O$, and in several naturally-occurring silicates, among them *asbestos*, $3MgSiO_3.CaSiO_3$, and *talc*, $H_2Mg_3(SiO_3)_4$. It occurs in small quantities in living matter, and is, for example, an essential constituent of chlorophyll, the green colouring-matter of plants.

Preparation.—Magnesium is prepared on the commercial scale by two processes. In the first the raw material is magnesium chloride hexahydrate, $MgCl_2.6H_2O$, from carnallite. This is melted in an iron pot, but to reduce the hydrolysis that normally takes place—$MgCl_2 + H_2O \rightleftharpoons MgO + 2HCl \uparrow$—it is first mixed with an equal weight of common salt; in this fused mixture the magnesium is possibly partly combined as a complex anion. The temperature is 700°. The melt is then electrolysed with the pot as cathode and a graphite anode suspended in it: so long as the magnesium concentration of the melt is kept up, magnesium will separate in preference to sodium. In the U.S.A. magnesium chloride is obtained from sea-water, dehydrated by heating in a current of hydrogen chloride, fused, and electrolysed.

In the second process the raw material is magnesium oxide. The electrolyte consists of equal parts of magnesium and barium fluorides to which sodium fluoride is added to lower the melting-point. Electrolysis is carried out at 950°, and the melt, which is contained in a steel vessel, forms a solid crust on the surface. The cast-iron cathodes project from the bottom of the vessel, while the carbon anodes are suspended in the liquid. The molten magnesium

produced at the cathode by electrolysis is lighter than the liquid and rises, but is protected from the air, in which it would burn at this temperature, by the solid crust of electrolyte, under which it collects.

From time to time magnesium oxide is added to the melt. Magnesium is much less electropositive than barium or sodium, and is preferentially deposited. The current is carried to the anode by both fluoride and oxide ions, but at that electrode only the latter are discharged, owing to the high discharge potential of fluoride ion. The net action is:

$$2MgO = 2Mg + O_2 \uparrow.$$

FIG. 116.   MAGNESIUM FROM MAGNESIUM OXIDE

There is therefore no loss of fluorine, and the magnesium fluoride need not be replenished. The product is about 99 per cent pure. The metal is now purified on a commercial scale by sublimation at 600° under a pressure of 1 mm. of mercury.

Uses.—Magnesium is used in flashlight powders and in the new light alloys such as magnalium: in the laboratory it is used as a reducing agent and in the preparation of the hydrides of boron and silicon. *Elektron*, an alloy with the very low density of 1·8, consists of 90 per cent magnesium alloyed with copper, zinc, manganese, and silicon. It is used for the crank-cases and gear-box casings of motor cars, and is protected from corrosion by an anodic oxidation process similar to that now applied to aluminium (p. 532). In spite of being highly inflammable, it can be welded.

Properties.—Magnesium is a white, fairly hard metal which in the laboratory is usually supplied in ribbon, filings, or powder. It is stable in dry air, but in moist air is slowly oxidized to the monoxide MgO. When heated it burns with the well-known blinding white light, the products being the monoxide with a little of the nitride Mg_3N_2. In the formation of this latter compound magnesium resembles lithium and also the alkaline-earth metals. The white cloud produced by flashlight powders is magnesium oxide. Magnesium reacts violently with acids, and slowly liberates hydrogen from hot water. The action is impeded by the film of insoluble hydroxide produced on the surface of the metal. Since magnesium hydroxide, for some reason not fully understood, is slightly more soluble in most salt solutions than in pure water,

solutions of such substances as sodium or calcium chlorides act on magnesium much more rapidly than pure water, especially if heated. Solutions of salts of weak bases (e.g. ammonium salts) also dissolve magnesium by reason of their acid reaction. Magnesium will burn brightly if heated in a current of steam:

$$Mg + 2H_2O = Mg(OH)_2 + H_2.$$
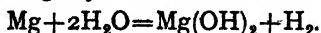
Magnesium is sometimes included with the elements calcium, strontium, and barium in the term 'alkaline-earth metals': the 'earth' is the oxide. Like these elements, magnesium is always bivalent: it is less electropositive than calcium, but much more so than zinc. It has only a very slight tendency to form complex ions, excluding, of course, the hydrated cation, though there is evidence of auto-complex formation in some of its solutions, e.g. those of magnesium sulphate. Double salts, often hydrated, are also common. Its compounds are nearly all hydrated, and in the absence of water there is a very marked tendency to form complexes. In the solid state we may mention the compound $MgCl_2.2NH_3$, which can be made even at $300°$, and in ethereal solution the interesting GRIGNARD compounds made by dissolving dry magnesium in a solution of a dry alkyl iodide, such as C_2H_5I, in dry ether:

$$Mg + C_2H_5I = Mg\begin{matrix} \diagup C_2H_5 \\ \diagdown I \end{matrix}$$
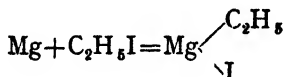
In their preparation it is necessary rigorously to exclude water, which hydrolyses them at once. In aqueous solution the only stable form of magnesium is the bivalent hydrated ion, and the hydroxide, $Mg(OH)_2$, is a strong base, though almost insoluble in water. The relation between magnesium and the alkaline-earth elements resembles that between lithium and the alkali-metals, and the two elements resemble each other, in accordance with the rule already alluded to (p. 479). Magnesium also resembles zinc, but can easily be separated from it by the solubility of zinc oxide in alkalis or by the insolubility of zinc sulphide.

The principal insoluble compounds of magnesium are the hydroxide, carbonate, fluoride, oxalate, phosphate, and double ammonium phosphate.

Oxide and Hydroxide.—Magnesium oxide, *magnesia*, MgO, is obtained by burning the metal in oxygen or by heating the hydroxide or carbonate. It is a colourless solid with a high melting-point used in one of the processes for magnesium manufacture, in furnace linings, and as the incandescent filament of the NERNST lamp. An impure oxide is obtained by heating magnesite, the naturally-occurring carbonate of magnesium, or by heating magnesium

chloride hexahydrate for a long time in the air. In contact with water it forms magnesium hydroxide, $Mg(OH)_2$, which can be reconverted to the oxide by heating for some time to 400° or over. The hydroxide is a colourless substance precipitated when caustic alkalis are added to magnesium salt solutions. It is almost insoluble in water (solubility-product about 10^{-11}) but is sufficiently soluble to affect indicators, and is a strong base with no trace of acid properties. It is less soluble in caustic alkalis than in water, a characteristic which links magnesium with the alkaline earths and distinguishes it from beryllium and zinc. Aqueous ammonia can be used instead of caustic alkali for the precipitation, but if sufficient excess of ammonium salt is also present the hydroxyl ion concentration of the solution is so much reduced that the solubility-product of the hydroxide is not exceeded and no precipitation takes place. To concentrated magnesium solutions a considerable excess of ammonium salt must be added if precipitation is to be prevented.

Magnesium hydroxide is soluble in acids to give magnesium salt solutions, and is also slightly soluble in solutions of ammonium salts, which have a slightly acid reaction from hydrolysis. The equilibrium is:

$$Mg(OH)_2 + 2NH_4 \cdot \rightleftharpoons 2NH_3 + 2H_2O + Mg\cdot\cdot.$$
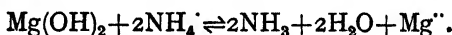
Calculations based on the law of mass-action show that this solubility is not due to the formation of a putative ammino-magnesium complex ion in appreciable concentration.

Peroxide.—Magnesium peroxide, MgO_2, is prepared by electrolytic oxidation of magnesium salt solutions or by the action of hydrogen peroxide on a suspension of the hydroxide. It is much less stable than the peroxides of the alkaline earths, and has never been prepared free from considerable quantities of water and the lower oxide.

Nitride.—Magnesium nitride, Mg_3N_2, is formed when a magnesium is heated in nitrogen. The metal becomes incandescent when heated in ammonia, and the same compound is produced:

$$3Mg + 2NH_3 = Mg_3N_2 + 3H_2.$$
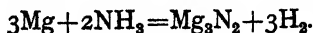
It is hydrolysed by water with the formation of magnesium hydroxide and ammonia:

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3.$$
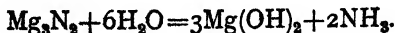
Carbonates.—Normal magnesium carbonate, $MgCO_3.3H_2O$, dissolves in water to the extent of about 1·8 gm. per litre at room temperature, and is so very much more soluble than the hydroxide

that a solution of sodium carbonate precipitates from solutions of magnesium salts a mixture of the carbonate and hydroxide, or possibly a basic carbonate. This substance can be converted to the normal carbonate by suspending it in water and passing carbon dioxide through the liquid. If the current of gas is continued too long, the whole of the precipitate redissolves as the soluble bicarbonate, $Mg(HCO_3)_2$.

Ammonium carbonate will produce no precipitate in solutions of magnesium salts containing ammonia and an ammonium salt in excess, if the concentration of the latter is sufficiently high. Solutions of ammonium salts have an acid reaction by hydrolysis, and this reduces the carbonate ion concentration from the action:

$$H^{\cdot} + CO_3'' \rightleftharpoons HCO_3'.$$
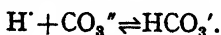
The carbonates of the alkaline earths, however, are considerably less soluble than magnesium carbonate, and are invariably precipitated under these conditions, a fact which is made use of in the separation of magnesium from these elements in qualitative analysis.

After heating for some time to, say, 750°, the conversion of magnesium carbonate to the oxide is complete; it is more easily decomposed by heat than the carbonates of the alkaline-earth metals.

Halides.—These compounds, except the insoluble fluoride, may be prepared in solution by the usual methods, but if the hydrates produced by evaporation are heated, hydrolysis takes place and oxyhalides or basic salts are produced. The anhydrous compounds (again except the fluoride) are best prepared by the action of the halogen or the hydrogen halide on the metal. When heated in air the fluoride is chemically unchanged, but the other halides are converted to oxides, e.g.:

$$2MgI_2 + O_2 = 2MgO + 2I_2.$$
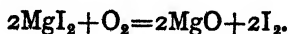
Magnesium fluoride also has a much higher melting-point (1400°) than have the other halides (about 700°).

Magnesium fluoride, MgF_2, is precipitated from magnesium salt solutions by soluble fluorides. It is used in one process of magnesium manufacture.

Magnesium chloride, $MgCl_2$, is prepared in large quantities as the hexahydrate, $MgCl_2.6H_2O$, by the evaporation of the mother liquors remaining when the potassium chloride has been removed from carnallite (p. 445). Together with the naturally-occurring carbonate *magnesite*, this is the source of most of the magnesium compounds of commerce. Magnesium chloride is also found in sea-water. It

is used in magnesium manufacture. It is very soluble in water, and on evaporation of the solution an oxychloride, $MgO.MgCl_2$, remains. A substance of similar composition is artificially prepared by mixing magnesium oxide, obtained by heating magnesite, with magnesium chloride hexahydrate, and is used as a cement; for when water is added to the finely-ground mixture it sets to a hard mass.

Magnesium bromide, $MgBr_2$, is found in sea-water; it forms various hydrates.

Magnesium perchlorate, $Mg(ClO_4)_2$, prepared from the hydroxide and perchloric acid, is a very efficient drying agent for gases. When it has absorbed much water it can be dried by heating to 240°.

Magnesium sulphide, MgS, is a substance which must be prepared in the dry way, as for instance by the union of the elements, since it is hydrolysed by water. Neither hydrogen sulphide nor ammonium sulphide produces any precipitate in solutions of magnesium salts, and if hydrogen sulphide is bubbled through a suspension of the hydroxide the latter dissolves to form the soluble hydrosulphide:

$$Mg(OH)_2 + 2H_2S \rightleftharpoons Mg^{..} + 2SH' + 2H_2O.$$
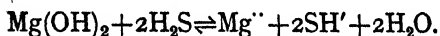
On boiling, the change is reversed: magnesium hydroxide is precipitated and hydrogen sulphide evolved.

Magnesium sulphate, $MgSO_4$, occurs native in the hydrated form as *kieserite*, $MgSO_4.H_2O$, and *Epsom salt*, $MgSO_4.7H_2O$. Solutions or hydrates can be made without difficulty by the usual methods, but if the attempt is made to drive off all the water of crystallization by heating, the substance begins to decompose into the oxide. Magnesium sulphate is used in medicine (as a purgative) and in dyeing.

Magnesium nitrate, $Mg(NO_3)_2.6H_2O$, can be prepared in solution, or in the form of various hydrates, by the usual methods; but, like the sulphate, it cannot be prepared in the anhydrous state.

Magnesium ammonium phosphate, $(NH_4)MgPO_4.6H_2O$, is a colourless compound precipitated from solutions of magnesium salts by ammonium dihydrogen phosphate, $(NH_4)H_2PO_4$. Magnesium is usually precipitated in this form for the purpose of quantitative analysis. On strong heating, magnesium pyrophosphate, $Mg_2P_2O_7$, remains and can be weighed:

$$2(NH_4)MgPO_4.6H_2O = Mg_2P_2O_7 + 2NH_3 \uparrow + 13H_2O \uparrow.$$

Magnesium boride (p. 522).
Magnesium silicide (p. 582).

SUBGROUP A

CALCIUM, STRONTIUM, BARIUM, [RADIUM]

Ca = 40·08.   *Atomic Number*, 20
Sr = 87·63.   *Atomic Number*, 38
Ba =137·36.   *Atomic Number*, 56
[Ra=225·97.   *Atomic Number*, 88]

History.—LAVOISIER suggested that all the substances known collectively as *earths* were in reality metallic oxides.   Davy (1808) prepared impure calcium by electrolysing lime in the presence of mercury as cathode, subsequently distilling off the mercury in a tube filled with petroleum vapour.   MOISSAN (1898) obtained metallic calcium of 99 per cent purity by strongly heating calcium iodide with sodium.

Strontia was recognized as a distinct earth in 1793 by HOPE, who obtained it from a mineral resembling heavy-spar (see below) found at Strontian in Argyllshire; CRAWFORD had tentatively advanced the same opinion three years earlier.   Metallic strontium, in an impure state, was prepared in 1808 by Davy, by electrolysis of the fused chloride.

Barium, in the form of its sulphate, was first mentioned by CASCIOROLUS in 1602 or 1603, who observed that the mineral heavy-spar ($BaSO_4$), when heated strongly with charcoal, yielded a substance that glowed in the dark.   This substance (impure BaS) was known as the ' Bolognan stone.'   SCHEELE (1774) concluded that a peculiar earth was the basis of heavy-spar, and DE MORVEAU suggested the name *barote* (afterwards changed to *baryta*) for it.   The impure metal was first obtained in 1808 by Davy, who electrolysed the fused chloride.

[For the history of *radium*, see p. 304.]

Occurrence.—*Calcium* is one of the most abundant of the elements, and occurs in nature chiefly as the carbonate, in the form of lime-stone, chalk,, marble, *calcite, aragonite, Iceland spar*, etc., or in combination with magnesium carbonate as *dolomite*, $CaCO_3.MgCO_3$. Calcium sulphate occurs in nature as *anhydrite*, $CaSO_4$, or in the hydrated form as *gypsum* or *alabaster*, both $CaSO_4.2H_2O$.   Calcium silicate is a constituent of many rocks.

Calcium is essential to the life of both animals and plants.   In animals it is contained chiefly in the bones, of which about four-fifths is calcium phosphate, and both calcium and phosphorus, though not, of course, in the elementary state, are given to children whose bone development is retarded.   Calcium fluoride is contained . the teeth, and causes them to fluoresce when exposed to X-rays.

Strontium is one of the less common elements, and is the least abundant of the alkaline-earth elements. The principal strontium minerals are *strontianite*, $SrCO_3$, and *celestine*, $SrSO_4$: they are widely distributed in small quantities.

Barium occurs fairly abundantly in nature as *witherite*, $BaCO_3$, or *barytes* or *heavy-spar*, $BaSO_4$, in many silicates, and in smaller quantities in other minerals. Barium compounds do not occur in noticeable quantities in the human body: indeed, they are poisonous.

After the alkali-metals, and excluding of course the inert gases, the metals of the alkaline earths are the most homogeneous subgroup of the periodic table. Like the alkali-metals, they are highly electropositive and chemically reactive, and they have low densities. The valency is always two and the tendency of the metal to ionization, as shown by its standard electrode potential, increases as usual with the atomic number, while the contrary applies to the tendency to form hydrates, covalent compounds, and complexes. The tendency to form complexes or covalent compounds is slight throughout the subgroup, but some calcium salts, such as the chloride or nitrate, have a high solubility in such solvents as the alcohols, which is much less marked with strontium and is absent with barium.

The solubility of the salts in water, expressed in gram-molecules per litre, in this group usually increases with the tendency to form hydrates, that is, from barium through strontium to calcium, but the solubilities of the hydroxides, fluorides, and oxalates (all salts of weak acids) lie in the reverse order, while the carbonate solubilities are irregular. Examples (solubilities in grams anhydrous salt per 100-gm. solution at 20°):

	Chloride	*Sulphate*	*Fluoride*
Calcium	43	·20	·0016
Strontium	35	·15	·012
Barium	26	·0002	·16

All the alkaline earths colour the Bunsen flame: calcium brick-red, strontium crimson, barium green. The two latter colours are used in fireworks.

Metals.—Calcium is now prepared on a large scale by electrolysis of the fused chloride. Since calcium chloride, when pure, melts at 780° and the metal at only 810°, the process offers great technical difficulties. These have been overcome only in recent years, by water-cooling the melt round the cathode, by withdrawing the cathode from the melt as it grows, and by using impure calcium chloride, which melts at a lower temperature. The nature of the

process will be clear from the diagram: the anode is the graphite lining of the containing vessel.

The other alkaline-earth metals have been made only in the laboratory. They are best prepared from the amalgam by distilling off the mercury in an inert atmosphere: a process which, as already mentioned, was first carried out by Sir Humphry Davy. The amalgam is prepared by electrolysing an aqueous solution of one of the salts with a mercury cathode. It is difficult to drive off all the mercury. The metals can also be prepared by heating the oxide or chloride with aluminium or sodium.
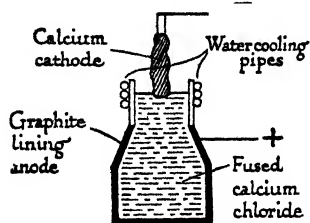
FIG. 117.   MANUFACTURE OF CALCIUM

The metals of the alkaline earths are silvery-white substances, rather harder than lead and with a low density. They are rapidly tarnished in air, forming surface layers of oxide and nitride, and burn brightly when heated in air or oxygen. They are chemically very reactive, resembling in this the alkali-metals, and liberate hydrogen vigorously from water, though the action of cold water on calcium is slow on account of the formation of a protective layer of hydroxide. They are powerful reducing agents, and will reduce hydrogen chloride to hydrogen, most metallic salts to the metal, carbon monoxide to carbon, and concentrated sulphuric acid to sulphur and sulphur dioxide or hydrogen sulphide.

Now that calcium can be obtained cheaply, it is coming into use in the laboratory as a reducing agent and for removing nitrogen or hydrogen from gases. In metallurgy it is used as a deoxidizer, and, together with aluminium, in the preparation of certain new light alloys. It is a convenient substance to use for the dehydration of alcohol.

Hydrides.—The alkaline-earth metals combine with hydrogen, slowly at room temperature and with incandescence on heating, forming hydrides of formula CaH_2, SrH_2, BaH_2. These are white crystalline substances with high melting-points, and are more easily formed than the alkali-metal hydrides. They can be melted in a hydrogen atmosphere without loss of weight, but at higher temperatures begin to dissociate. The hydrides of the alkaline earths increase in stability with increasing atomic number of the metal, whereas the reverse is true of the alkali-metal hydrides. They are electrovalent and contain *negative* hydrogen; thus the electrolysis of fused calcium hydride yields calcium at the cathode and hydrogen at the *anode* (compare lithium hydride, p. 436).

They can be gently heated in air without alteration, but at a red heat burn brilliantly, forming the oxide of the metal and steam:

$$CaH_2+O_2=CaO+H_2O.$$
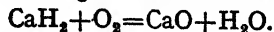
With water they liberate in all twice as much hydrogen as they contain:

$$CaH_2+2H_2O=Ca(OH)_2+2H_2 \uparrow,$$
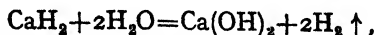
and the heat developed is sometimes enough to ignite the hydrogen. On strongly heating the hydrides in nitrogen the nitrides are obtained, e.g.:

$$3BaH_2+N_2=Ba_3N_2+3H_2.$$
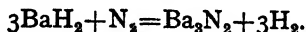
The hydrides are very powerful reducing agents.

Oxides and Hydroxides.—The oxides are usually prepared by heating the carbonates, a process sometimes described as ' burning ' them:

$$CaCO_3 \rightleftharpoons CaO+CO_2 \uparrow.$$
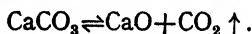
At room temperature the equilibrium pressure of carbon dioxide over all the carbonates is very minute—much less than the partial pressure of carbon dioxide in ordinary air—and at this temperature the oxides will readily combine with carbon dioxide, the action being nearly complete. The equilibrium pressure of carbon dioxide over calcium carbonate reaches 760 mm. at 890°, but strontium and barium carbonates require a higher temperature, and their decomposition is usually assisted by adding a reducing agent such as carbon. The carbonates can of course be decomposed at much lower temperatures if the carbon dioxide is allowed to leave the system as it is produced.

Calcium oxide, ' quicklime,' is produced industrially by heating limestone in a lime-kiln, which is often heated by producer-gas. The process can be made continuous, limestone being added at the top and lime withdrawn at the bottom. When quicklime is mixed with a little water a vigorous action takes place and sufficient heat is liberated to boil some of the water: a dry powder of calcium hydroxide, ' slaked lime,' $Ca(OH)_2$, remains. If the quicklime contains much magnesium oxide, or if it has been heated to a very high temperature, combination with water takes place only slowly. The oxides of strontium and barium likewise combine with water to form hydroxides, which, unlike calcium hydroxide, form stable hydrates such as $Ba(OH)_2.8H_2O$.

The oxides of the alkaline-earth metals are white solids with very high melting- and boiling-points: calcium oxide melts at 2550° and boils (in the electric arc) at about 3400°. When heated in the oxy-hydrogen flame it remains solid and gives out a very bright white light, the ' limelight.' The oxides can be reduced only with the greatest difficulty.

The hydroxides differ greatly in their solubility in water. The solubility in grams of hydroxide (unhydrated) per 100 gm. solution at 20° is as follows: $Ca(OH)_2$, 0·16; $Sr(OH)_2$, 0·61; $Ba(OH)_2$, 1·7. The solubility of calcium hydroxide decreases with rising temperature, whereas the solubilities of strontium and barium hydroxides increase, and the latter is very soluble in hot water. All the hydroxides are sufficiently insoluble to be precipitated from their cold solutions by caustic alkali, if the concentrations are high enough; the solution of calcium hydroxide is called 'lime-water,' that of barium hydroxide 'baryta.' The hydroxides all retain water tenaciously. Slaked lime is converted to quicklime at a red-heat, but barium hydroxide requires a temperature of about 900° for reasonably rapid conversion. All the hydroxides are strong bases, and baryta is used as a volumetric reagent, but it must be protected from the carbon dioxide of the air, which precipitates barium carbonate. For the same reason baryta is the best solution for the preparation of pure hydrogen by electrolysis.

In the laboratory calcium oxide is used to remove water from substances which combine with calcium chloride, e.g. ammonia or alcohol. For this purpose it should be freshly heated before use. When required in industry it is usually manufactured on the spot. It is used in the manufacture of sodium carbonate (SOLVAY process), caustic soda from sodium carbonate, calcium carbide, bleaching powder, glass, mortar, cement, and other materials; and as a furnace lining. *Mortar* is a mixture of calcium oxide, water, and sand; it is freshly made just before use, and sets in the air to a complex mixture of calcium carbonate and silicate. *Portland cement* was invented in 1824 by a bricklayer named ASPDIN; it is made by strongly heating a mixture of limestone and clay in the proportion of about three to one. The product is ground fine and when mixed with water rapidly sets to a hard mass.

Soda-lime is made by mixing powdered lime with molten caustic soda; it is a mixture of sodium hydroxide with calcium oxide and hydroxide. It does not deliquesce like caustic soda and is a convenient absorbent for carbon dioxide. In the war of 1914-18 it was used in gas masks to absorb chlorine.

Strontium oxide is used in the purification of sugar from molasses, from which it precipitates an insoluble compound, 'strontium saccharate.' This is washed and decomposed by carbon dioxide and water:

'Strontium saccharate '+carbon dioxide=sugar+strontium carbonate.
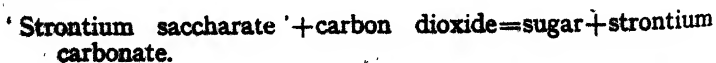
The less soluble strontium carbonate is removed from the solution

and the strontium oxide is recovered by heating it. Calcium oxide has been used for the same purpose, but calcium saccharate is more soluble. The use of barium is undesirable on account of the poisonous properties of barium salts.

Peroxides.—All the alkaline-earth metals form peroxides of formula MO_2, insoluble or slightly soluble in water, and precipitated from solutions of salts of the alkaline earths by hydrogen peroxide in alkaline (e.g. ammoniacal) solutions, or by a solution of sodium peroxide:

$$Ca^{..} + H_2O_2 + 2OH' = CaO_2 \downarrow + 2H_2O.$$
$$Ca^{..} + Na_2O_2 = CaO_2 \downarrow + 2Na^{.}.$$
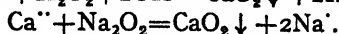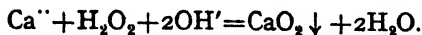
All are white solids that on strong heating decompose into oxygen and the normal oxide, but very different temperatures are required. While the pressure of oxygen in equilibrium with calcium and strontium oxides exceeds one atmosphere at low temperatures, with barium oxide a pressure of one-fifth of an atmosphere is not reached till about 700°. Consequently the peroxides of calcium and strontium are decomposed by heating (calcium peroxide decomposes rapidly at 280°), whereas barium peroxide is stable in air up to about 700°, when the equilibrium pressure of oxygen is equal to the partial pressure of oxygen in the atmosphere. At lower temperatures barium oxide will take up oxygen from the air, though the velocity of this reaction at room temperature is immeasurably small. At about 100° it is, however, fairly rapid, and this was the basis of the old BRIN process for oxygen manufacture. Barium peroxide was made by gently heating barium oxide in the air and then decomposed by reducing the pressure, which was cheaper than heating to above 700°.

When precipitated from cold solutions all the peroxides appear as octa-hydrates such as $BaO_2.8H_2O$. They are insoluble in alkalis, but with acids give hydrogen peroxide and a salt:

$$BaO_2 + 2H^{.} = Ba^{..} + H_2O_2.$$
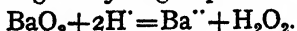
This reaction was formerly used in the preparation of hydrogen peroxide. When barium peroxide is treated with dilute sulphuric acid it is converted to the much less soluble barium sulphate, but the action is a slow one and slightly reversible:

$$BaO_2 \downarrow + H_2SO_4 \rightleftharpoons BaSO_4 \downarrow + H_2O_2.$$
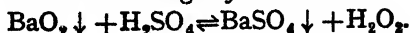
Barium peroxide can be estimated by treating it with ferricyanides, with which mutual reduction takes place, the products being oxygen and a ferrocyanide:

$$BaO_2 + 2Fe(CN)_6''' = Ba^{..} + O_2 \uparrow + 2Fe(CN)_6''''.$$

Carbonates.—The carbonates of all the alkaline-earth metals occur in nature. Calcium carbonate occurs in several forms which

have already been mentioned.   Among them is Iceland spar, which is sometimes found in fine large crystals remarkable for double refraction.   The decomposition of limestone by heat is the source of most of the carbon dioxide and quicklime of commerce.   In the laboratory carbon dioxide is prepared by treating lumps of marble with dilute acids, often in Kipp's apparatus: if a powdered form of the carbonate is used, the evolution of gas is inconveniently rapid.

All three carbonates are nearly insoluble in water, strontium carbonate being the least soluble and calcium carbonate the most; but a litre of a saturated solution of the latter at room temperature contains only about 0·02 gm.   They are therefore precipitated when soluble carbonates are added to alkaline-earth salt solutions, and can be precipitated from these solutions by carbon dioxide if the solutions are sufficiently alkaline for the carbonate ion concentration to reach a reasonable value:

$$CO_2 + 2OH' \rightleftharpoons CO_3'' + H_2O.$$
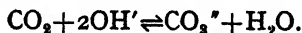
A solution of lime-water fulfils this condition, but no calcium carbonate can be precipitated by carbon dioxide at atmospheric pressure from a solution of, say, calcium chloride.   The solubility of calcium hydroxide so greatly exceeds that of calcium carbonate that the former can be nearly completely converted to the latter by carbon dioxide and water or by carbonates: this is the basis of one method for making caustic soda from sodium carbonate (p. 438):

$$Ca(OH)_2 \downarrow + CO_3'' \rightleftharpoons CaCO_3 \downarrow + 2OH'.$$
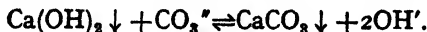
The calcium carbonate precipitated by carbon dioxide from lime-water is seen to redissolve if the stream of gas is continued.   This is due to the formation of the soluble bicarbonate, $Ca(HCO_3)_2$, as follows:

$$CaCO_3 \downarrow + CO_2 + H_2O \rightleftharpoons Ca\cdot\cdot + 2HCO_3'.$$

If the solution is boiled it decomposes, like all bicarbonate solutions, and the carbonate is reprecipitated; the action represented by the equation just given simply goes in the opposite direction.   This is because the active mass of the carbon dioxide in the solution is extremely small owing to the low solubility of the gas in hot water.

Nitrides.—These compounds are prepared by heating the element in nitrogen.   They have formulae such as Ca_3N_2, and are decomposed by water or steam with the formation of ammonia:

$$Ca_3N_2 + 6H_2O = 2NH_3 \uparrow + 3Ca(OH)_2$$

Halides.—The halides of the alkaline-earth metals are salts can be prepared by the usual methods.   With the exception the fluorides, they all show evidence of covalency, though in main they are electrovalent compounds.   The evidence for

covalency is (1) considerable variation with dilution of the transport number; (2) solubility in organic solvents; (3) low melting-point in comparison with the fluoride. This tendency is much more pronounced with calcium than with barium; strontium is intermediate but inclines to calcium. The melting-points, some of which are based on rather uncertain data, are shown in the table (in degrees C.):

	Fluoride	Chloride	Bromide	Iodide
Calcium	1330	780	760	740
Strontium	> 1450°	870	640	500
Barium	1280	960	880	740

In the nearly insoluble fluorides the solubility increases from calcium to barium, in the other halides the reverse order is followed.

Fluorides.—Calcium fluoride, CaF_2, occurs in nature as crystals of *fluorspar*, sometimes brilliantly coloured and in Derbyshire known as ' blue john ' or ' green john.' It is the principal source of fluorine compounds, and is also used in some optical apparatus, as it is transparent in the infra-red and ultra-violet regions of the spectrum.

The solubility of all three fluorides is very slight, and they can be precipitated with a soluble fluoride from solutions of salts of the alkaline-earth metals. Calcium fluoride is sufficiently insoluble to be used in the quantitative analysis of fluorides.

Chlorides.—Calcium chloride, $CaCl_2$, is produced in very large quantities as a by-product of several industrial processes, notably the Solvay process. It is exceedingly soluble in water, with which it forms hydrates containing one, two, four, and six molecules of water per molecule of calcium chloride. Its solubility in gram-molecules per litre is so high that it is often used in the preparation of freezing-mixtures; the eutectic mixture freezes at −55° and contains about 40 gm. anhydrous salt per 100 gm. water. A saturated solution boils at 180°. Calcium chloride has been used for melting ice on the streets. It deliquesces rapidly in the air, and is much used in the laboratory as a drying agent for gases, though it is not as efficient as sulphuric acid or phosphorus pentoxide. It cannot be used for drying ammonia, as it combines avidly with the gas, forming a compound $CaCl_2.8NH_3$. Similarly, it must not be employed in drying amines, such as aniline. Formerly a waste product of chemical industry, it now finds a wide range of industrial and commercial applications.

The transport number of the chloride ion in calcium chloride solutions varies from 0·55 in very dilute solutions to 0·72 in concentrated ones, and this is evidence for the existence of undissociated molecules or complex ions. Strontium and barium chlorides show less variation. Calcium chloride is very soluble in the alcohols.

with which it forms molecular compounds; strontium chloride is less soluble and barium chloride scarcely dissolves at all.

When the chlorides are fused in air, a trace of oxide is found in the product; this is due not to hydrolysis but to reaction with atmospheric oxygen:

$$2CaCl_2 + O_2 = 2CaO + 2Cl_2.$$
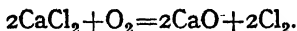
The change is most marked with calcium and least marked with barium.

If anhydrous calcium chloride is dissolved in water heat is given out, and it might be supposed from LE CHATELIER's rule that the solubility would decrease with rising temperature. This is not so, as the solution at this temperature is in equilibrium not with the anhydrous salt, but with the hexahydrate. If the heat of formation of the hexahydrate from the anhydrous salt is subtracted from the total heat of solution, the result is negative; and heat is absorbed, as would be expected, when the hexahydrate dissolves.

The bromides and iodides are all very soluble in water, and all form hydrates. The calcium and strontium salts dissolve in alcohol, but the barium salts are less soluble.

Bleaching-powder is a rather dirty white powder made by the action of chlorine upon *nearly dry* slaked lime (the proportion of moisture is not allowed to exceed 4 per cent). In BACHMANN's process the slaked lime is blown to the top of a chlorinating tower by means of compressed air, and is distributed to the highest floor of the tower through a hopper. It then falls to successive lower floors, on each of which it is mechanically raked, while a current of chlorine is driven up the tower in the opposite direction. Conditions are so adjusted that by the time the product reaches the last floor it is fully chlorinated. Hot air is now blown through it to remove free chlorine, and the bleaching-powder falls into a hopper from which it can be delivered into containers.

Bleaching-powder (' chloride of lime ') is a mixture of *calcium hypochlorite*, $Ca(OCl)_2$, with *basic calcium chloride monohydrate*, $CaCl_2.Ca(OH)_2.H_2O$. Its formation may be represented by the equation:

$$3Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2.Ca(OH)_2.H_2O + H_2O.$$
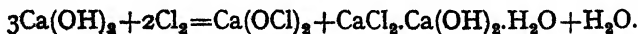
The main reaction is, however, accompanied by side-reactions, so that impurities are always present. These include calcium chlorate, $Ca(ClO_3)_2$, and calcium chloride tetrahydrate, $CaCl_2.4H_2O$, as well as some unchanged slaked lime.

When dilute acids act upon bleaching-powder, chlorine is evolved:

$$Ca(OCl)_2 + CaCl_2.Ca(OH)_2.H_2O + 3H_2SO_4 = 3CaSO_4 + 5H_2O + 2Cl_2$$
$$Ca(OCl)_2 + CaCl_2.Ca(OH)_2.H_2O + 6HCl = 3CaCl_2 + 5H_2O + 2Cl_2.$$
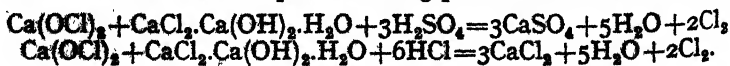
A calculation will show that a mixture of the composition assigned to bleaching-powder should liberate 41 per cent of its weight of chlorine, and this is the approximate actual yield from a very good specimen. The ordinary commercial product contains 36–40 per cent of such ' available ' chlorine, i.e. chlorine set free by the action of a dilute acid. If the lime is insufficiently chlorinated, the product naturally contains a lower percentage of available chlorine.

On exposure to air, bleaching-powder gradually loses chlorine, owing to the action of carbonic acid (atmospheric moisture and carbon dioxide):

$$Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HClO$$
$$2HClO = 2HCl + O_2$$
$$HClO + HCl = H_2O + Cl_2.$$
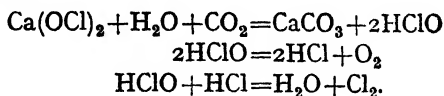
It should therefore be preserved in air-tight tins or bottles; but even so it slowly deteriorates, partly by loss of oxygen from the hypochlorite:

$$Ca(OCl)_2 = CaCl_2 + O_2,$$
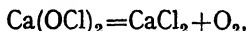
and partly by spontaneous conversion of the hypochlorite into chlorate and chloride:

$$3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2.$$
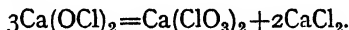
The decomposition of the hypochlorite into chloride and oxygen is catalysed by cobalt salts. If a suspension of bleaching-powder is heated with a little cobalt nitrate solution a vigorous evolution of oxygen occurs. It is thought that the mechanism of this catalysis may be the alternate formation and decomposition of cobalt peroxide:

$$2CoO + Ca(OCl)_2 = 2CoO_2 + CaCl_2$$
$$2CoO_2 = 2CoO + O_2.$$
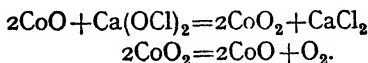
The original cobaltous oxide, CoO, is formed by the action of the lime in the bleaching-powder:

$$Co(NO_3)_2 + Ca(OH)_2 = CoO + Ca(NO_3)_2 + H_2O.$$
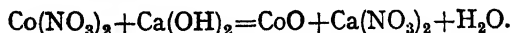
A fabric to be bleached is steeped in a dilute solution of bleaching-powder and then exposed to the air for some time. Atmospheric ' carbonic acid ' liberates hypochlorous acid, $HClO$, from the bleaching-powder, and this destroys the colouring matter. The fabric is then rinsed in water acidified with a little sulphuric acid, to decompose any unchanged bleaching-powder, and is afterwards placed in an antichlor bath. Finally it is thoroughly washed in water.

The available chlorine in bleaching-powder may be estimated by taking a known weight of the sample, mixing it in solution with excess of potassium iodide, and acidifying with acetic acid. The chlorine liberated from the bleaching-powder by the acid displaces from the iodide an equivalent weight of iodine, which can be estimated with standard sodium thiosulphate:

$$\text{I litre N/Ic Na}_2\text{S}_2\text{O}_3 \equiv 12 \cdot 7 \text{ gm. I} \equiv 3 \cdot 55 \text{ gm. chlorine.}$$

Owing to its strong oxidizing power, bleaching-powder is a good germicide and is widely used as a disinfectant.

Calcium iodate, $Ca(IO_3)_2$, is used as a preservative of food. It is more efficient than boric acid, and is good for the health, which boric acid is not.

Sulphides.—These compounds are prepared (i) by union of the elements; (ii) by heating the oxide in a stream of hydrogen sulphide (the action is reversible):

$$CaO + H_2S \rightleftharpoons CaS + H_2O;$$
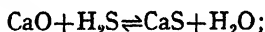
(iii) by reducing the sulphates, as for instance with carbon. This reaction is used in the preparation of barium compounds from the insoluble heavy-spar ($BaSO_4$), which is heated with coal:

$$BaSO_4 + 4C = BaS + 4CO \uparrow.$$
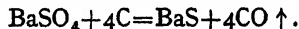
The mass is then extracted with water and the barium goes into solution as hydrosulphide:

$$2BaS + 2H_2O = 2Ba^{\cdot\cdot} + 2SH' + 2OH'.$$

Hydrosulphides such as $Ca(SH)_2$ are also produced in solution when hydrogen sulphide is passed into suspensions or solutions of the hydroxides:

$$H_2S + OH' = HS' + H_2O.$$
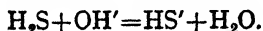
The monosulphides are colourless solids that have the power of glowing in the dark if certain impurities are present; the pure sulphides do not phosphoresce. The monosulphides are almost insoluble in cold water, but if the temperature is raised they are hydrolysed, the first products being hydrosulphides. Hydrosulphide solutions are decomposed on boiling into hydroxide and hydrogen sulphide:

$$HS' + H_2O = H_2S \uparrow + OH'.$$

Calcium sulphide is slowly oxidized to thiosulphate by air and water, and most of the sodium thiosulphate of commerce is obtained in this way from the calcium sulphide which is a by-product of the old LEBLANC process for the manufacture of washing-soda. When

heated in oxygen, the sulphides of the alkaline-earth metals are easily converted to sulphates:

$$CaS + 2O_2 = CaSO_4.$$
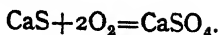
Polysulphides such as CaS_4 or CaS_5 can be obtained by boiling the sulphide or hydrosulphide solutions with sulphur. The alkalimetals and ammonium, whose monosulphides are also soluble in water, form similar compounds, which appear to contain neutral sulphur atoms combined with a bivalent sulphide ion to form a bivalent complex ion.

Sulphates.—All three sulphates occur native, and as they are all nearly insoluble in water they can also be precipitated by soluble sulphates from solutions of alkaline-earth salts. The approximate solubilities have already been given (p. 489). A saturated solution of calcium sulphate will form a precipitate with barium solutions or reasonably concentrated strontium solutions, and is used in distinguishing these elements from calcium. Barium sulphate is a very insoluble substance and is much used in quantitative analysis. It is, however, soluble in concentrated sulphuric acid (150 gm. per litre in the 98-per-cent acid at 25°), with which it forms the hydrogen sulphate, $Ba(HSO_4)_2$.

When gypsum, $CaSO_4.2H_2O$, the naturally-occurring dihydrate of calcium sulphate, is heated at 110° it is converted to the hemihydrate $2CaSO_4.H_2O$, called *plaster of Paris*. If this substance, in the form of a very fine powder, is mixed to a paste with water, it soon swells a little and sets to a hard mass of the dihydrate. This property is put to use in making casts of objects and in making plaster for other purposes. If too strongly heated, say at 200°, gypsum is converted to anhydrous calcium sulphate, which takes up water only very slowly and is not suitable for the preparation of quick-setting plaster.

Natural anhydrite is used in the manufacture of ammonium sulphate from synthetic ammonia. A saturated solution of ammonia is agitated with finely-powdered anhydrite, $CaSO_4$, while carbon dioxide is bubbled through the liquid, forming a carbonate, since the ammonia keeps it alkaline. The solubility of calcium sulphate at the working temperature is about a hundred times that of calcium carbonate, so the action:

$$CaSO_4 \downarrow + CO_3'' \rightleftharpoons CaCO_3 \downarrow + SO_4'',$$
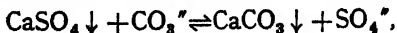
goes almost wholly to the right. The calcium carbonate is removed, and used to make calcium nitrate with synthetic nitric acid, while the ammonium sulphate is recovered from the solution by evaporation. This process is used at Billingham-on-Tees.

Nitrates.—The nitrates, such as $Ca(NO_3)_2$, are prepared by the

usual methods, and calcium nitrate is prepared on the large scale, as described above, for use as a fertilizer. Since barium nitrate is not very soluble in water, it can be precipitated from concentrated barium solutions by nitric acid or other soluble nitrates, but strontium and calcium nitrates are both deliquescent and exceedingly soluble in water. The high solubility of the calcium salt is a disadvantage when it is used as a fertilizer, as it is so quickly washed from the soil by rain. Calcium nitrate is also very soluble in the alcohols, whereas strontium and barium nitrates are nearly insoluble. All three nitrates decompose on strong heating, giving a mixture of gases and the oxide of the metal.

Phosphates.—Calcium orthophosphate, $Ca_3(PO_4)_2$, occurs in bones and is found native in various parts of the world, especially in Tunis and the United States. Guano, the droppings of sea-birds, after long exposure to the atmosphere consists principally of calcium phosphate. Calcium phosphate is a valuable manure, but since the mineral forms of the substance are insoluble in water the crushed ore is converted by sulphuric acid to a mixture of calcium sulphate and *calcium superphosphate*, a substance with the formula $CaH_4(PO_4)_2$, which is soluble in water:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$
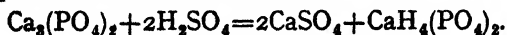
The mixture is sold and applied direct to the land.

Calcium phosphate (from bone-ash) is used in the manufacture of phosphorus (p. 616) and of table salt (p. 446). The normal phosphates of strontium and barium are likewise insoluble, and all three are precipitated by soluble phosphates from solutions of salts of the metals.

Chromates.—Barium chromate, $BaCrO_4$, is practically insoluble, strontium chromate very slightly soluble, and calcium chromate fairly soluble. At 18° the solubilities in grams per litre are: $BaCrO_4$ 0·004, $SrCrO_4$ 1·2, $CaCrO_4$ 23·2. This is made use of in the separation of the elements of the subgroup.

Separation of the Alkaline-earth Metals.—The principal methods are based on:

(i) The insolubility of barium chromate.

(ii) The insolubility of calcium fluoride.

(iii) The insolubility of barium sulphate.

(iv) The insolubility of strontium and barium nitrates in alcohol, in which calcium nitrate is soluble.

The insolubility of calcium oxalate is also frequently made use of in analysis.

SUBGROUP B

ZINC, CADMIUM, MERCURY

Zn = 65·38. *Atomic Number*, 30
Cd = 112·41. *Atomic Number*, 48
Hg = 200·61. *Atomic Number*, 80

The general characteristics of the subgroup have already been discussed: but there is a much wider variation between the elements than occurs in Subgroup A. Cadmium resembles zinc much more than it does mercury, which is in many respects unique among the elements, and must be separately considered. The principal complexes, excluding auto-complexes, are those with ammonia (e.g. $Zn.4NH_3^{\cdot\cdot}$ or $Hg.2NH_3^{\cdot\cdot}$), with cyanides (e.g. $Zn(CN)_4''$ or undissociated $Hg(CN)_2$), and with halides (e.g. CdI_4'' or HgI_4'').

The compounds of all these elements are poisonous, especially those of mercury.

ZINC AND CADMIUM

History.—Though brass was known at least a thousand years before the Christian era, the term *zinc*, as the name for a distinct metal, seems to have been invented by PARACELSUS (1493–1541). In his *Liber mineralium* he says that ' there is another metal, *zinckum*, which is in general unknown to the fraternity,' but admits that he is as yet unacquainted with its *ultima materia.* HENCKEL (1720) prepared metallic zinc comparatively free from impurities, and by 1740 CHAMPION had established at Bristol a works for extracting the metal from calamine ($ZnCO_3$).

Cadmia (CdO) was discovered by STROHMEYER in 1817, in the dust in the condensers of a zinc works at Salzgitter. KARSTEN (1819) showed that the new element was present in the zinc ores of Silesia, and the metal itself was shortly afterwards prepared by Strohmeyer by reduction of the oxide with charcoal.

Occurrence.—Zinc is an abundant element produced principally in the United States, Germany, Great Britain, Poland, and Belgium, where it occurs as *zinc spar* or *calamine*, $ZnCO_3$; *zinc blende*, ZnS; *willemite*, Zn_2SiO_4, and in other minerals. Cadmium is much less common; nearly all the cadmium of commerce is extracted from zinc ores, and the only important cadmium mineral is *greenockite*, CdS.

Extraction.—Zinc ores are first roasted in the air. The sulphide is converted to oxide, and evolves sulphur dioxide, which in large works is sometimes recovered, while the carbonate is also converted to oxide with the loss of carbon dioxide:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2. \qquad ZnCO_3 = ZnO + CO_2.$$
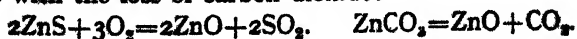
The silicate loses the water associated with it. This treatment also helps to remove any arsenic or antimony in the ores as the volatile oxides.

The product of the first operation is mixed with coal and distilled in small fireclay retorts which are heated by producer-gas. The
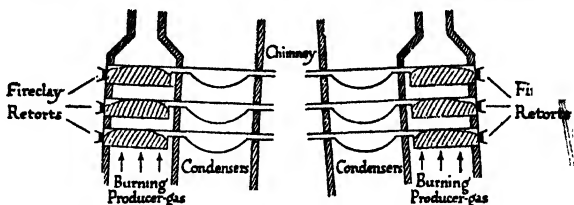
FIG. 118. ZINC DISTILLATION (DIAGRAMMATIC)

zinc distils over and is collected in iron condensers luted (i.e. cemented) to the retorts, while the carbon monoxide passes up the chimney:

$$ZnO + C = Zn + CO \uparrow.$$
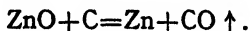
It usually burns at the mouth of the condenser, and the appearance of the flame helps the works engineer to follow the progress of the distillation.

The zinc obtained in this way is then refined by electrolysis. The standard electrode potential of zinc is -0.76 volts ($H_2 = 0$), but the over-voltage of hydrogen on a smooth zinc cathode nearly reaches this figure, and consequently zinc can be electrolytically deposited if the acidity of the solution is kept low enough.

Cadmium boils at 780° and zinc at 920°, so that when zinc ores containing cadmium are distilled the first fraction consists almost entirely of cadmium. A good deal of cadmium oxide is also commonly found in the condenser, so the distillate is mixed with coal and again fractionally distilled.

Metals.—Commercial *zinc* ('spelter') contains cadmium, iron, lead, and sometimes arsenic. It is difficult to purify, but may be distilled *in vacuo* or purified electrolytically. The volatile zinc ethyl, $Zn(C_2H_5)_2$, has also been used in the preparation of pure zinc compounds.

Crystals of pure *cadmium* may be obtained by adding zinc, which precipitates the less electropositive cadmium from its solutions, to a solution of a good specimen of cadmium sulphate.

The metals are greyish-white and are fairly soft, especially if pure. The physical properties of zinc depend very much on its state of purity, and this also affects the velocity of chemical changes in which it takes part. It is supplied to the laboratory as foil, as

zinc dust, or as granulated zinc, obtained by pouring molten zinc into water. Zinc is tolerably malleable, but must be warmed before it is drawn into wire.

Zinc and cadmium are stable in dry air, but in moist air become coated with a film of oxide and carbonate which prevents further attack of the metal. Iron is protected from rusting by covering it with a layer of zinc; this is done either electrolytically or by dipping the iron in molten zinc, and the product is called 'galvanized iron.' In the air molten zinc and cadmium are quickly covered with a layer of oxide, and if heated in oxygen they will burn. They will slowly decompose boiling water, but they soon become covered with a film of hydroxide, and zinc will not readily liberate hydrogen from any dilute solution—acid or alkaline— if the metal is very pure. This is connected with the high over-voltage of hydrogen at a zinc cathode, for which no explanation is quite generally accepted.

Zinc and cadmium dissolve in acids to form solutions of their salts, and will also dissolve slowly in solutions of caustic alkalis, but cadmium is not attacked to the same extent as zinc. Both metals will liberate a little hydrogen from solutions of ammonium salts, forming complex ions $(Zn.4NH_3)^{..}$ and $(Cd.6NH_3)^{..}$. With hot concentrated sulphuric acid, sulphur and hydrogen sulphide or sulphur dioxide are obtained.

Uses.—Zinc is used in the manufacture of galvanized iron, in alloys such as brass and coinage metals, and in electric batteries; it is the cheapest of the more electropositive metals. In the laboratory it is used as a reducing agent, chiefly in analytical and organic chemistry. Cadmium finds a limited use in the manufacture of fusible alloys, of standard cells, and in plating the bright parts of motor cars and bicycles. Cadmium is tougher and less easily corroded than zinc.

Oxides and Hydroxides.—The oxides are obtained by burning the metal in air or oxygen, or by heating the hydroxide or carbonate. Zinc oxide, ZnO, is white; it becomes yellow on heating but loses its colour again on cooling. Cadmium oxide, CdO, is brown. Both oxides are stable compounds which can be reduced by hydrogen only with difficulty. Zinc oxide is used in paints and ointments: zinc oxide paint, unlike white lead, is not affected in colour by hydrogen sulphide, as zinc sulphide is white. The very finely-divided form obtained by burning the metal in air is the best for making paint.

The hydroxides $Zn(OH)_2$ and $Cd(OH)_2$ are colourless compounds precipitated from zinc or cadmium solutions by caustic alkalis. They are readily converted to oxides when heated to 300° or over. They are practically insoluble in water. Both of them will dissolve

in acids to form solutions of zinc or cadmium salts. Zinc hydroxide has also distinct acidic properties, and when precipitated by caustic alkalis will dissolve in excess of the reagent, forming a zincate:

$$Zn(OH)_2 + 2OH' \rightleftharpoons ZnO_2'' + 2H_2O.$$
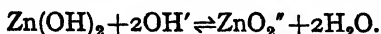
The solutions are decomposed on boiling and zinc hydroxide is deposited. By adding alcohol to solutions of zinc hydroxide in very concentrated caustic potash, crystals of *potassium zincate*, K_2ZnO_2, can be obtained; they are hydrolysed by water. The same compound can be prepared by fusing a mixture of zinc oxide and caustic potash:

$$ZnO + 2KOH = K_2ZnO_2 + H_2O \uparrow.$$

Cadmium hydroxide is not sufficiently acidic to dissolve in aqueous alkalis, but cadmiates resembling the zincates can be obtained by fusing cadmium oxide with solid caustic potash. Both zinc and cadmium hydroxides are slightly soluble in aqueous ammonia, but it can be shown that this is not due to the increased hydroxyl ion concentration of the solution and the resulting formation of zincates or cadmiates, since

(i) the hydroxyl ion concentration of the ammonia solution is much less than that of caustic alkali solutions too weak to dissolve cadmium hydroxide;

(ii) solutions of the substituted ammonias such as $(C_2H_5)_4NOH$, which are stronger bases than ammonia, have a smaller solvent effect;

(iii) on electrolysis the zinc concentration increases round the cathode, and not round the anode, as would be expected were one of the ionic species ZnO_2'', and as does actually happen in solutions of an alkali-metal zincate.

It is therefore inferred that the oxides have dissolved to form complex ions, and the law of mass-action applied to the solubility-relations shows these ions to be chiefly $(Zn.4NH_3)^{\cdot\cdot}$ and $(Cd.6NH_3)^{\cdot\cdot}$.

Peroxides.—When hydrogen peroxide is added to zinc hydroxide and water, a substance is obtained which may be $ZnO.H_2O_2$ but is more probably $ZnO_2.H_2O$. It is not very stable, and on heating readily loses oxygen: cadmium peroxide is similar. Neither can be prepared free from water and the lower oxide. With acids they yield hydrogen peroxide and a solution of a salt of zinc or cadmium.

Carbonates.—Zinc carbonate occures native (p. 501). It is the final product of the action of moist air on zinc. The carbonates of both zinc and cadmium are much less soluble than, for example, magnesium carbonate, and may be precipitated fairly pure by adding

soluble carbonates to solutions of their salts under suitable conditions, but the product always contains a little hydroxide. This may be avoided by passing carbon dioxide through the solution, or by using sodium hydrogen carbonate, whose solutions are much more acid than those of sodium carbonate, for the precipitation. Both carbonates are readily converted to the oxides on heating.

Halides.—Solutions of the halides of zinc and cadmium may be prepared by the usual methods, but on evaporation of these solutions (except that of the fluoride) hydrates are obtained which lose halogen acid by hydrolysis on further heating, leaving a basic salt, though this is much more marked with zinc than with cadmium, for the low dissociation of cadmium salts reduces their hydrolysis. The anhydrous halides must therefore be prepared by the action of the halogen or the hydrogen halide on the metal. All the anhydrous salts except the fluoride are converted to the oxide on heating in air. They are all soluble in organic solvents, the fluoride again excepted, and are very soluble in water; the fluorides are slightly soluble. The salts have a very great tendency to auto-complex formation and are probably partly covalent. In methyl alcohol, so far as they have been examined, they are weak electrolytes. Except the fluorides, they form numerous hydrates and have a great avidity for water. The solutions are markedly acid from hydrolysis. The melting-points are given below in degrees Centigrade: note the high values for the fluorides as compared with the remainder:

	Fluoride	Chloride	Bromide	Iodide
Zinc	872	283	394	446
Cadmium	1110	568	583	388

Chlorides.—Zinc powder or thin zinc foil will burn spontaneously in chlorine, forming the anhydrous chloride, $ZnCl_2$, a glassy, very hygroscopic substance used in the laboratory as a desiccating agent. *Cadmium chloride* is a crystalline substance which can also be prepared by the union of the elements. Several hydrates of both salts are known, and the anhydrous compounds combine avidly with ammonia to form compounds, $ZnCl_2.6NH_3$ and $CdCl_2.6NH_3$. Double compounds, such as $2KCl.ZnCl_2$ or $2KCl.CdCl_2.7H_2O$, are also very common in the solid state. Zinc chloride solutions, if sufficiently concentrated, will dissolve cellulose; on diluting the solution with water, the cellulose is reprecipitated. This was formerly used in the manufacture of carbon filaments for electric lamps by a squirting process followed by incomplete combustion. Solutions of zinc chloride, which is poisonous, like all zinc salts, are used in preserving wooden sleepers.

By heating either the anhydrous or the hydrated salts in air or oxygen numerous oxychlorides can be obtained, and a cement used for stopping teeth, and similar to magnesium oxychloride cement, is made from a mixture of zinc oxide and zinc chloride.

Bromides.—Pure zinc bromide was used by RICHARDS and ROGERS in the determination of the atomic weight of zinc. It was prepared by the union of the purified elements, and further purified by distillation at about 700° in an inert atmosphere.

Iodides.—Zinc and cadmium iodides are well known for auto-complex formation. The transport-number of the cadmium ion in concentrated solutions of the iodide, as calculated from migration experiments, has a large negative value, so much of the cadmium travels to the *anode* in the form of complex ions such as CdI_4''.

Sulphides.—Zinc sulphide, ZnS, occurs native as *blende*. The precipitation of the sulphides of zinc and cadmium by hydrogen sulphide has already been discussed (p. 196). Zinc sulphide is white and cadmium sulphide primrose yellow; the latter is used as a pigment. In the presence of certain impurities, zinc sulphide phosphoresces, and is used on screens in experiments on radioactivity. The pure substance has not this power.

Sulphates.—The sulphates are colourless compounds which can be obtained by the usual methods: the hydrates in equilibrium with the saturated solution at room temperature are $ZnSO_4.7H_2O$ and $3CdSO_4.8H_2O$. Unlike magnesium sulphate, the sulphates of zinc and cadmium can be dehydrated without decomposition. They are both very soluble in water: the solubility of the cadmium salt has a low temperature-coefficient round about room temperature, and it is used in Weston cells (p. 248). The principal use of zinc sulphate is in the manufacture of *lithopone,* a white pigment consisting of a mixture of barium sulphate and zinc sulphide. It is prepared as a precipitate by mixing solutions of zinc sulphate and barium sulphide.

Nitrates.—These can be prepared by the usual methods in the form of several hydrates, but it is doubtful whether all the water of hydration can be removed without decomposing the salt, which readily loses nitric acid on heating. The hydrates both of zinc and cadmium nitrates are very soluble in water and also dissolve without difficulty in alcohol.

Phosphates.—Zinc and cadmium resemble magnesium in the formation of an insoluble compound ($(NH_4)ZnPO_4$ and $(NH_4)CdPO_4$) when solutions of their salts are treated with a solution of ammonium dihydrogen phosphate, $(NH_4)H_2PO_4$. On heating the precipitate, the pyrophosphates $Zn_2P_2O_7$ and $Cd_2P_2O_7$ are obtained, and this process is used in the gravimetric analysis of zinc and cadmium.

Separation of Zinc and Cadmium.—Zinc and cadmium compounds may be separated

(i) by electro-deposition of the cadmium (p. 266);

(ii) by precipitation of the cadmium as sulphide (p. 196);

(iii) by extracting the mixed hydroxides with aqueous caustic potash;

and by other methods.

MERCURY

The principal differences between mercury and the other members of the subgroup are its low melting-point, high density, and positive electrode potential, the predominantly covalent character of most of the mercuric compounds, and the existence of a whole series of organic compounds and of the mercurous salts and the amalgams.

History.—Mercury has been known in the elementary state since very early times; thus a small vessel filled with mercury was found by SCHLIEMANN in a grave considered to be of the sixteenth or fifteenth century B.C. PLINY (first century A.D.) distinguishes between the native metal, which he calls *argentum vivum* ('quicksilver'), and *hydrargyrum* ('liquid silver') prepared from cinnabar (HgS) by powdering the latter with vinegar in a copper vessel. This method of extraction was mentioned by THEOPHRASTUS in his book on *Stones,* about 300 B.C. Among the alchemists, mercury was frequently regarded as the seed of all metals, while the alternative theory, which regarded metals as compounds of mercury with sulphur, was commonly accepted for a period of over a thousand years (see Historical Introduction). The fact that mercury is definitely a metal was confirmed by BRAUN (1759–1760), who observed that it could be frozen in a freezing-mixture.

Occurrence.—Mercury is one of the scarcer elements. The most important deposits are in California, at Almaden (Spain), in Idria, and in Mexico, where the mercury occurs as the sulphide *cinnabar,* HgS, mixed with small quantities of the native element.

Extraction.—There are two processes for extracting mercury from cinnabar. They are both carried out at temperatures above the boiling-point of the element, so that it distils over and can be collected in condensers. In the first process the cinnabar is roasted in air:

$$HgS + O_2 = Hg \uparrow + SO_2 \uparrow.$$
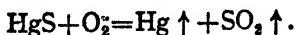
In the second the ore is mixed with quicklime and heated in retorts in the absence of air. A mixture of calcium sulphide and sulphate remains in the retort:

$$4HgS + 4CaO = 4Hg \uparrow + 3CaS + CaSO_4.$$
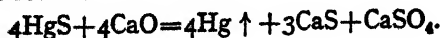
At Almaden, in Spain, where the first process has been worked for centuries, the condensers originally designed in 1633 in Peru are still in use; they are small earthenware cylinders called *aludels*, and are arranged in rows.

Purification.—The first step is to filter the mercury through chamois leather, an operation first described by PLINY. The more electropositive metals, such as zinc, cadmium, or lead, are then removed by passing the metal in a rain of small drops through very dilute nitric acid: the operation can be made continuous if the apparatus is combined with an air-lift attached to a filter-pump. The metal is then dried with filter-paper and again filtered through leather, and is then distilled in a vacuum or in carbon dioxide under low pressure.

Metal.—Mercury is a heavy grey liquid, density 13·59, freezing at −39° and boiling at 360°. The vapour is monatomic. The metal is appreciably volatile even at ordinary temperatures. It is stable in the air, but is slowly converted on heating to the oxide HgO. It is attacked by ozone, which covers it with a thin film of oxide and causes it to ' tail '—i.e. to adhere in small flecks to a glass surface. It will not reduce steam.

Mercury is unaffected by dilute hydrochloric or sulphuric acid, but dissolves in the hot concentrated acids to give hydrogen and sulphur dioxide respectively. It is unaffected by very dilute nitric acid, but with fairly concentrated acid pure nitric oxide can be obtained, with mercurous nitrate in solution:

$$6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 2NO \uparrow + 4H_2O.$$
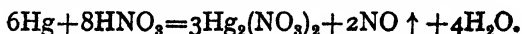
Mercury reacts vigorously with the halogens in the cold.

The metal is used in scientific instruments and laboratory apparatus (e.g. the pneumatic trough), and in the electrical industry. It is the international standard of resistance. Fairly large quantities are used in some types of electrolytic cell (p. 438). Mercury was formerly used in the extraction of gold and silver by the amalgam process. Constipation was formerly treated by giving the patient a pound or two of mercury to swallow, and mercury ointment is still used in the treatment of certain diseases.

Oxides.—The hydroxides of mercury are very unstable and need not be considered here: indeed, their existence is open to doubt.

Mercurous oxide, Hg_2O, is a black substance, insoluble in water, prepared by the addition of caustic alkalis to solutions of mercurous salts. It is an unstable compound that slowly absorbs oxygen from the air to form mercuric oxide, and by heat or light is readily decomposed into mercuric oxide and mercury.

Mercuric oxide, HgO, can be prepared by heating mercury in air or oxygen, but this method is very slow. It can also be made by

heating mercuric nitrate, or precipitated by caustic alkalis from solutions of mercuric chloride.

It occurs in two forms, one red, the other yellow. As the red variety can be converted to the yellow by grinding, it is probable that the difference in colour is due to a difference in the size of the grains. On heating to about 650°, the oxide is decomposed into oxygen and mercury, which volatilizes; this is in marked contrast with the behaviour of the oxides of other Group II elements. It is also easily reduced to the metal by hydrogen on warming or by carbon monoxide in the cold.

The oxide, which is almost insoluble in water, dissolves in acids to give solutions of mercuric salts, but shows only the feeblest acidic properties. It does not dissolve to any significant extent in aqueous alkalis, and the products obtained by dissolving it in fused alkalis at high temperatures cannot exist in presence of water. The oxide is, however, distinctly soluble in solutions of the alkali-metal chlorides, bromides, and iodides—the solubility increases in that order—and application of the law of mass-action shows the equilibrium to be:

$$HgO + 4I' + H_2O \rightleftharpoons HgI_4'' + 2OH'.$$
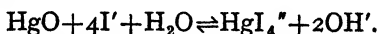
This has been made use of in the preparation of solutions of standard alkalinity in volumetric analysis. A known weight of mercuric oxide is dissolved in excess of aqueous potassium iodide, and two gram-ions of hydroxyl are produced for every gram-molecule of mercuric oxide dissolved.

Mercury peroxide, HgO_2.—This compound can be obtained by the action of aqueous hydrogen peroxide on mixed alcoholic solutions of mercuric chloride and potassium hydroxide. It is a red compound which slowly decomposes, especially in the presence of water, into mercuric oxide and oxygen, but it is fairly stable when dry, and in this condition can be kept for a few days at room temperature.

THE MERCUROUS COMPOUNDS.—*Preparation*.—The mercurous compounds, in which the valency of the metal appears to be 1, are prepared by the action of acids on mercury, by direct combination with mercury in excess, or by reduction of the mercuric compounds, often with metallic mercury as the reducing agent.

Constitution.—If mercury is really univalent in these compounds, they are the only example of soluble compounds of Group II elements in which the metal has a valency other than 2. It is true that the molecular weight of mercurous chloride as calculated from the vapour density is in agreement with the single molecule HgCl, but this can equally well be explained by complete dissociation of the vapour into mercury and mercuric chloride:

$$Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2.$$

The vapour density of the thoroughly dried substance is in closer agreement with the double formula. The question was finally decided by OGG, who proved that the mercurous ion was a complex formed by the combination of a mercuric ion with an atom of mercury:

$$Hg^{\cdot\cdot} + Hg \rightleftharpoons Hg_2^{\cdot\cdot},$$
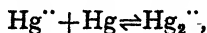
and consequently that the valency of mercury in the mercurous compounds was 2. The evidence was as follows:

Electrochemical Evidence.—1. The valency type of an electrolyte can be inferred from the effect of dilution on the E.M.F. of a concentration cell (p. 262). Thus the electrode potential of a metal A in a solution containing ions A$^{\cdot}$ changes by 0·058 volts on tenfold dilution of the electrolyte, while if the ions are A$^{\cdot\cdot}$ the change is only half this amount. In this way the valency of the mercurous ion in a solution of mercurous nitrate was shown to be 2.

2. The slope of the curve connecting the equivalent conductivity of mercurous nitrate with the square root of the concentration is about equal to that usual for other bi-univalent salts.

Evidence from Freezing-points.—3. The freezing-points of solutions of mercurous nitrate in dilute nitric acid (necessary to prevent hydrolysis) are in agreement with the existence of $Hg_2^{\cdot\cdot}$ ions.

Evidence from the Law of Mass-action.—4. A solution of mercuric nitrate will dissolve some mercury and an equilibrium is set up between mercurous and mercuric ions, which on the alternative views must be represented:

$$Hg + Hg^{\cdot\cdot} \rightleftharpoons 2Hg^{\cdot} \quad \text{or} \quad Hg + Hg^{\cdot\cdot} \rightleftharpoons Hg_2^{\cdot\cdot}.$$
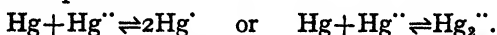
If the former is correct $\dfrac{[Hg^{\cdot}]^2}{[Hg^{\cdot\cdot}]}$ should be a constant, if the latter, $\dfrac{[Hg_2^{\cdot\cdot}]}{[Hg^{\cdot\cdot}]}$. The mercurous salt concentration at equilibrium, as determined by analysis, is found to be nearly proportional to the mercuric salt concentration, and not to its square root, so the second view is correct.

5. Mercury will reduce a solution of silver nitrate to silver, which forms an amalgam, until the mercurous ion concentration of the solution reaches an equilibrium value. The action may be represented:

$$Hg + Ag^{\cdot} \rightleftharpoons Hg^{\cdot} + Ag \quad \text{or} \quad 2Hg + 2Ag^{\cdot} \rightleftharpoons Hg_2^{\cdot\cdot} + 2Ag,$$

and the equilibrium expressions will be $\dfrac{[Hg^{\cdot}]\,[Ag]}{[Ag^{\cdot}]}$ and $\dfrac{[Hg_2^{\cdot\cdot}]\,[Ag]^2}{[Ag^{\cdot}]^2}$, where [Ag] represents the concentration of silver in the amalgam. The second expression is found to be approximately constant: the former is not.

Properties.—With respect to the mercurous ion, mercury has a fairly high positive standard potential (+0·80 volts), and the mercurous salts of easily discharged anions (such as the iodide ion) cannot exist in water except at very low concentration, i.e. they are insoluble. The same applies to the mercurous salts of weak acids. The only important soluble mercurous salts are the fluoride and the salts of such oxyacids as the nitrate, chlorate, and perchlorate. These salts are extensively ionized in aqueous solution, but unless acid is added to them they are liable to undergo hydrolysis with deposition of basic salts. The mercurous salts do not show the remarkably strong tendency to covalency of the mercuric compounds: they are dissociated in solution, and mercury in the mercurous condition will neither form organic compounds nor readily form complex ions: it is already a complex ion itself.

The mercurous salts are easily reduced to mercury or oxidized to mercuric salts. In the presence of mercury the balanced action

$$Hg_2^{\cdot\cdot} \rightleftharpoons Hg \downarrow + Hg^{\cdot\cdot}$$
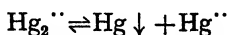
reaches (at 25°) an equilibrium in which the concentration of mercurous salt is about 240 times the concentration of mercuric salt. Mercuric salts are therefore nearly completely reduced by mercury, but mercurous salts, on the other hand, are decomposed by substances which absorb mercuric ions to form complex ions, undissociated molecules, or very insoluble substances such as mercuric sulphide, HgS (whose solubility-product is only about 10^{-54}). This explains the precipitation of mercury from solutions of mercurous compounds by ammonia, cyanides, and sulphides:

$$Hg_2^{\cdot\cdot} + 2NH_3 \rightarrow Hg \downarrow + (Hg.2NH_3)^{\cdot\cdot}.$$
$$Hg_2^{\cdot\cdot} + 2CN' \rightarrow Hg \downarrow + Hg(CN)_2 \text{ (unionized)}.$$
$$Hg_2^{\cdot\cdot} + S'' \rightarrow Hg \downarrow + HgS \downarrow.$$
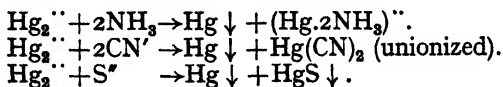
Mercurous carbonate, Hg_2CO_3, is a yellow substance obtained by precipitating solutions of mercurous salts with sodium hydrogen carbonate. It readily decomposes, especially if warmed, into mercury, mercuric oxide, and carbon dioxide:

$$Hg_2CO_3 \rightarrow Hg + HgO + CO_2 \uparrow.$$
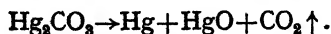
Halides.—The fluoride is the only soluble mercurous halide; the other anions are too easily discharged for the salts to be stable in solution except at low concentrations.

Mercurous fluoride, Hg_2F_2, can be obtained by the action of hydrogen fluoride on mercurous carbonate. It is soluble in water.

**R

Mercurous chloride, calomel, Hg_2Cl_2, is a white substance precipitated from mercurous solutions by soluble chlorides, or obtained by heating a mixture of mercury and mercuric chloride until the calomel sublimes. Apart from the evidence quoted above, X-ray analysis confirms the structure Hg_2Cl_2. It is practically insoluble in water. It can easily be sublimed by heating, as the vapour pressure reaches 760 mm. at 373°. The vapour is completely dissociated into mercury and mercuric chloride unless the substance has been thoroughly dried, when less dissociation takes place. Mercurous chloride is blackened by aqueous ammonia, and is converted to a mixture of mercury and mercuric amino-chloride:

$$Hg_2Cl_2+2NH_3=Hg\downarrow+Hg(NH_2)Cl\downarrow+NH_4^{\cdot}+Cl'.$$
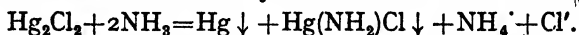
Calomel is used in medicine as a purge, and in ointments.

Mercurous bromide, Hg_2Br_2, is a white insoluble substance precipitated from mercurous salt solutions by soluble bromides, and

Mercurous iodide, Hg_2I_2, is prepared in a similar way. It is a somewhat unstable yellow substance insoluble in water and other solvents.

Mercurous sulphate, Hg_2SO_4, is produced together with mercuric sulphate when mercury is boiled with strong sulphuric acid, but is best prepared by precipitating a solution of a mercurous salt with sulphuric acid; it is insoluble in water. It is a white substance which on long boiling with water is converted by partial hydrolysis to a basic salt.

Mercurous nitrate, $Hg_2(NO_3)_2$, the most important soluble mercurous salt, is obtained by the action of cold not too dilute nitric acid on mercury, and freed from a little mercuric nitrate by recrystallization. Unlike the majority of mercury compounds, it forms a hydrate, $Hg_2(NO_3)_2.2H_2O$, which, however, loses water in the air. The solution of mercurous nitrate used in the laboratory usually contains free nitric acid added to prevent hydrolysis.

THE MERCURIC COMPOUNDS.—In these compounds the tendency to covalency already remarked in zinc and still more in cadmium has reached a degree unknown in any other definitely metallic element. Mercury forms a large number of organic compounds, far more than any other metal, and such a substance as mercury methyl, $Hg(CH_3)_2$, is scarcely attacked by water. The mercuric ion has a great tendency to form undissociated molecules and complex ions. Excluding the mercurous compounds already discussed, the principal mercuric complexes are with ammonia, $(Hg.2NH_3)^{\cdot\cdot}$; cyanides, $Hg(CN)_2$ (unionized); halides, HgI_4'', unionized $HgCl_2$, etc. It is, however, remarkable that the mercuric compounds do not readily form hydrates. The principal insoluble salts are the carbonate, sulphide, iodide, sulphate, and

phosphate. The soluble salts, as regards their ionization in aqueous solution, fall into three classes:

(i) The fluoride and the salts of the strong oxyacids (e.g. nitrate or perchlorate) are highly dissociated.

(ii) The remaining halides are only slightly dissociated. They are volatile compounds, and the chloride and bromide are very soluble in organic solvents.

(iii) The salts of weak acids are practically undissociated: the classical example is the cyanide, $Hg(CN)_2$. The concentration of mercuric ions in solutions of this substance is so low that the addition of caustic alkali precipitates no mercuric oxide.

Mercuric oxide is rather weakly basic, so that all the soluble mercuric salts are hydrolysed in solution and have an acid reaction, except those of class (iii), whose mercuric ion concentration is too small for hydrolysis to be noticeable.

It seems that mercury has a great reluctance to form compounds in which it has a covalency of more than two. The reason for this behaviour is unknown, but some such explanation is necessary to account for the rarity of hydrated mercuric salts.

Mercuric carbonate, $HgCO_3$.—It is doubtful whether this compound has ever been obtained in the pure state. Carbonates or hydrogen carbonates of the alkali-metals precipitate basic carbonates from mercuric solutions.

Halides.—These salts are all rather slightly soluble in cold water, and the iodide is almost insoluble. The melting-points are: fluoride, 645°; chloride, 265°; bromide, 236°; iodide, 250°. The fluoride is predominantly electrovalent, the others are mainly covalent. Only the highly dissociated fluoride is sufficiently hydrolysed to make its preparation from the aqueous solution a matter of difficulty. The chloride and bromide can be obtained by evaporation, and the iodide by precipitation.

Mercuric fluoride, HgF_2, is best obtained by heating mercurous fluoride:

$$Hg_2F_2 = Hg \uparrow + HgF_2.$$
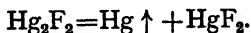
Evaporation of its solutions gives a mixture of the fluoride and oxide.

Mercuric chloride, corrosive sublimate, $HgCl_2$, can be obtained by the usual methods. When mercury burns in chlorine, either mercurous or mercuric chloride is produced according to whether the metal or the gas is in excess. Mercuric chloride is a colourless crystalline substance which can easily be purified by distillation in a stream of chlorine. It melts at 265° and boils at 300°. It is prepared on a commercial scale by direct synthesis, or sometimes

by distillation of a mixture of mercurous sulphate and common salt, to which a little manganese dioxide is added as an oxidizing agent to prevent the formation of mercurous chloride. The ionization of its aqueous solutions is very slight, indeed for most purposes negligible, and appears from transport-number measurements to take place in steps, of which the first is:

$$HgCl_2 \rightleftharpoons HgCl^{\cdot} + Cl'.$$

At ordinary dilutions the degree of dissociation, based on this change, is of the order of 0·05 per cent, and by far the largest part of the solute is in the form of undissociated molecules.

Mercuric chloride readily dissolves in a large number of organic liquids, such as ether, acetone, or toluene. Its distribution-ratio between toluene and water is of the order of unity, a very unusual circumstance for a metallic salt, and measurements on this system have been used to confirm the absence of dissociation indicated by the feeble conducting power of the aqueous solution. Mercuric chloride is very much more soluble in hot water than in cold.

Mercuric chloride is easily reduced to mercurous chloride or to mercury. Hydrogen peroxide *reduces* it in alkaline solution (best obtained from sodium peroxide and water) to the metal:

$$HgCl_2 + Na_2O_2 = Hg \downarrow + O_2 \uparrow + 2Na^{\cdot} + 2Cl',$$
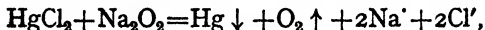
whereas in neutral solution, with Rochelle salt as catalyst, calomel is precipitated:

$$2HgCl_2 + H_2O_2 = Hg_2Cl_2 \downarrow + O_2 \uparrow + 2H^{\cdot} + 2Cl'.$$
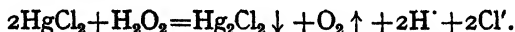
With ammonia a white precipitate of mercuric amino-chloride, $Hg(NH_2)Cl$, is obtained:

$$HgCl_2 + 2NH_3 = Hg(NH_2)Cl \downarrow + NH_4Cl.$$
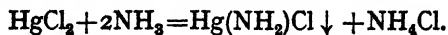
Like all the mercuric compounds, corrosive sublimate is a powerful poison: it is used in taxidermy and in preventing the growth of fungi and bacteria in water, e.g. in thermostats.

Mercuric iodide, HgI_2.—When a solution of an iodide, such as potassium iodide, is added to the solution of a mercuric salt, a brilliant scarlet precipitate of mercuric iodide is produced which very readily dissolves in excess of iodide to give a colourless solution containing all the mercury in the anion:

$$Hg^{\cdot\cdot} + 2I' = HgI_2 \downarrow . \quad HgI_2 \downarrow + 2I' = HgI_4''.$$
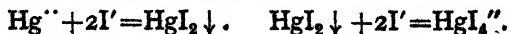
Mercuric iodide can also be prepared by mixing mercury with excess of iodine: the action takes place spontaneously in the cold. The substance exists in two forms, one bright red form, which is stable

up to 128°, and another bright yellow form stable from 128° upwards. The yellow form can be undercooled, but below 128° reverts to the stable red form when rubbed with a crystal of the red substance. As usually happens, the yellow or less stable form is the first to be precipitated from solution, and this can sometimes be observed when a soluble iodide is added to a mercuric solution, but the change to the red form is very rapid.

Although almost insoluble in water, mercuric iodide has a distinct solubility in many organic liquids such as the alcohols or toluene. From a concentrated solution in excess of potassium iodide solution, crystals of the compound K_2HgI_4, potassium mercuri-iodide can be obtained, and also a compound $KHgI_3$, corresponding with the ion HgI_3'. The solutions do not contain a sufficient concentration of mercuric ions to give a precipitate of mercuric oxide with caustic alkalis. A solution which has been made alkaline is called *Nessler's solution*, and is the most sensitive test known for ammonia or ammonium compounds, with which it gives a brown precipitate, or, with very dilute solutions, a yellow coloration. The exact composition of the precipitate is uncertain, but is probably $(NH_2Hg_2I_3)$.

Mercuric sulphide, HgS, is an exceedingly insoluble substance which occurs native as *cinnabar*, and can be precipitated from mercuric solutions by soluble sulphides. It exists in two forms: an unstable black form which is the first to be precipitated from solution, and a stable red form into which the black form is converted on heating. The red form is used as a pigment under the name of *vermilion*; it is always artificially prepared, usually by heating mercury and sulphur together. Mercuric sulphide can be sublimed without difficulty, but it is much less volatile than the halides. It is so insoluble that it is only slowly attacked even by strong acids in concentrated solution.

Mercuric sulphate, $HgSO_4$, is made by the action of sulphuric acid on mercuric compounds, or by dissolving mercury in hot concentrated sulphuric acid and evaporating repeatedly to dryness, replenishing the acid; this is to decompose the mercurous sulphate which is simultaneously produced. Mercuric sulphate is converted to a basic salt by water: but it will dissolve in sulphuric acid, in which it is contained probably as mercuric hydrogen sulphate, $Hg(HSO_4)_2$. It is a colourless substance which is used as a catalyst in certain organic reactions; e.g. the manufacture of acetaldehyde from acetylene.

Mercuric nitrate, $Hg(NO_3)_2$, is obtained by the action of nitric acid on mercuric oxide, or by boiling mercury for some time with concentrated nitric acid in excess and thereby oxidizing the mercurous nitrate first produced. It is a colourless hygroscopic

substance which crystallizes as $2Hg(NO_3)_2.H_2O$ and $Hg(NO_3)_2.H_2O$. It is very soluble in water and the solutions are dissociated and strongly hydrolysed: unless free acid is added to them they deposit basic nitrates on evaporation.

Mercuric cyanide, $Hg(CN)_2$, is made from mercuric oxide and hydrogen cyanide. It is a colourless substance soluble in water, in which it is undissociated. On heating, it yields mercury and cyanogen:

$$Hg(CN)_2 = Hg + (CN)_2 \uparrow,$$
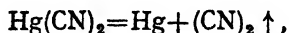
together with some paracyanogen (p. 579). It is exceedingly poisonous.

Amalgams.—Nearly all metals dissolve to some extent in mercury or combine with it, and the products are called *amalgams.* They may be liquids or solids, and they may consist of solutions of the metal (in the atomic form, as is shown by freezing-point measurements) in mercury, or of definite compounds between the metal and mercury, or of solutions of such compounds in mercury. They are prepared by direct combination (e.g. sodium amalgam), or by electrolysis of a concentrated solution of a salt of the metal with a mercury cathode (e.g. ammonium or barium amalgam), or by reducing such a solution with mercury (e.g. silver amalgam), or by reducing a solution of a mercuric salt with the metal (e.g. aluminium amalgam). Amalgams of highly electropositive metals such as sodium can be prepared by the electrolytic method in contact with water by reason of two facts: (1) that the electrode potential of the metal is diminished when it is, so to speak, ' diluted ' with mercury, and (2) that the over-voltage of hydrogen on a mercury or amalgam cathode is high. Nevertheless, the preparation of such amalgams by the electrolytic method is usually accompanied by the evolution of hydrogen.

It is often possible to isolate from amalgams crystalline compounds between the metal and mercury, but their composition seems to bear little or no relation to the valency of the metal. Thus among the compounds between sodium and mercury, $NaHg$, $NaHg_2$, $NaHg_8$, Na_3Hg, and others have been isolated. When it is not possible to isolate the compound, its existence can often be inferred from the freezing- and melting-point lines of the phase diagram, or from discontinuities in the curve connecting the vapour pressure of mercury over the amalgam with its composition. Amalgams are easily decomposed, and with respect to their chemical properties they behave like a solution of the metal in mercury.

Sodium amalgam.—Sodium reacts with mercury with the evolution of heat and light. The amalgam is readily oxidized in air and

is decomposed by water, but it can be prepared by the electrolysis of concentrated solutions of sodium salts with a mercury cathode, and this is made use of in one process for the manufacture of caustic soda (p. 437). It is used as a reducing agent, chiefly in organic chemistry, as it is less violent in its action on water than sodium itself. Amalgams of some of the less electropositive metals can be prepared by treating solutions of their salts with sodium amalgam, e.g.:

$$2Na\ amalgam + Ba^{..} \rightleftharpoons Ba\ amalgam + 2Na^{.}.$$
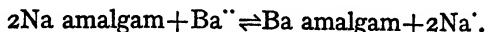
Copper, silver, and gold amalgams are readily formed by direct combination, as can easily be seen by rubbing a clean coin with mercury. Silver amalgam can also be made by reducing silver nitrate solutions with mercury. The amalgams of silver and gold have been used in the extraction of those metals from their ores.

The Amalgams of strontium and barium have been used in the preparation of the metals (p. 490). The amalgams can be prepared, though with difficulty, by electrolysis.

Aluminium amalgam.—If aluminium foil is warmed with a solution of mercuric chloride it becomes covered with a layer of the amalgam. Some mercurous chloride is produced at the same time. The chemical activity of the aluminium is much increased by amalgamation: it will readily liberate hydrogen from water and is the best available drying agent for the alcohols. The amalgamated foil rapidly oxidizes in the air, a process attended by the evolution of much heat, so that a minute or two after withdrawing it from the solution it may be too hot to hold.

Tin amalgam is used as a backing for mirrors.

' *Ammonium amalgam.*'—When a concentrated solution of ammonium chloride is electrolysed with a mercury cathode, the mercury swells up into a mass which has the consistency of butter and behaves as though it were an amalgam of the free radical ammonium. The same substance can be obtained by the action of sodium amalgam on a concentrated solution of ammonium chloride. When removed from the solution the amalgam slowly decomposes, yielding mercury, ammonia, and hydrogen.
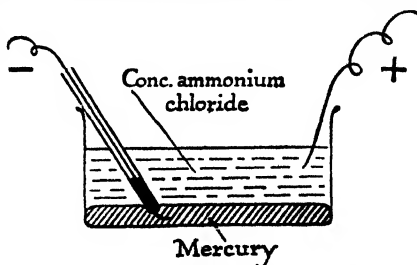
FIG. 119. PREPARATION OF AMMONIUM AMALGAM

In the light of modern electronic theory of valency there are grave difficulties in recognizing a free radical of the formula NH_4, because if all the N,H bonds are of the common or normal electron-pair type then the nitrogen nucleus must bind nine electrons, which is one electron in excess of the maximum possible for an element in the series Li—F (see p. 335).

CHAPTER XVII

GROUP III AND THE RARE EARTHS

BORON, ALUMINIUM, SCANDIUM, YTTRIUM, LANTHANUM, AND
RARE EARTH METALS, GALLIUM, INDIUM, THALLIUM

B—Al⟨ Sc—Y—La and Rare Earth Metals
         Ga—In—Tl
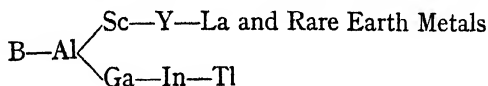
| Element | Typical Elements | | Subgroup | | | |
| | | | A | B | | |
	B	Al	Sc	Ga	In	Tl
Atomic Number	5	13	21	31	49.	81
Atomic Weight	10·82	26·98	44·96	69·72	114·82	204·39
Density	2·34	2·70	3·9	5·89	7·3	11·9
Atomic Volume	4·6	10·0	11·6	11·9	15·7	17·3
Melting-point	2200–2500°	659°	1200°	30°	155°	302°

PROPERTIES OF SOME GROUP III ELEMENTS

IN Group III the typical elements and the subgroups resemble each other much more closely than in Group II, but on the whole the typical elements must be associated with Subgroup A (which contains the rare-earth group, unique in the periodic table) rather than with Subgroup B.

Boron differs from the other elements of the group and resembles silicon. It is a non-metal which does not conduct electricity, has a very small atomic volume, forms no cation, and has a very high melting-point. It is unique in the group in forming a series of covalent hydrides with highly complex structures, and its hydroxide is a weak acid while the other hydroxides are predominantly basic. All the other Group III elements are metals, more electropositive than hydrogen, which will dissolve in dilute acids or even in water. With the typical elements and Subgroup A, valencies other than three are very uncommon, being practically confined to a few of the rare earths. The hydroxides become more basic from the weakly acidic boron hydroxide, through the amphoteric but chiefly basic aluminium hydroxide, to the fairly strong basic hydroxides of the rare earths, while the salts such as the chlorides range from the purely covalent boron trichloride to

the electrovalent chlorides of the rare earths. However, even the rare earth trichlorides are soluble in alcohol and hydrolysed to some extent by evaporation of their aqueous solutions. The sulphides are all decomposed by water.

Subgroup B differs from Subgroup A in the lower atomic volumes of the elements; their trihydroxides are weaker bases. Subgroup B elements are also remarkable for their low melting-points and for the occurrence of lower valencies as follows: *gallium*, very unstable valency of one; *indium*, possibly valency of two and very unstable valency of one; *thallium*, one is the most stable valency. These elements much resemble their neighbours in the B subgroups of Groups II and IV, and the resemblance is particularly noticeable if the thallous salts are compared with the mercurous or plumbous salts.

The valency groups of the tervalent compounds of all Group III elements contain six electrons, and these compounds are vigorous acceptors. Many of them are associated in the vapour phase or in solution, and they form additive compounds with most donor substances, as, for instance, ammonia.

Among Group III elements, only boron and aluminium are abundant or of commercial importance.

BORON

B=10·82.   *Atomic Number,* 5

History.—The word *borax* is derived from the Arabic *buraq* ('white and shining'), a term applied to many substances used by the Moslem chemists as fluxes. One such substance, *tincal* or *tincar* or *attincar*, obtained from India, Armenia, and Tibet, is the compound $Na_2B_4O_7.10H_2O$, to which the name 'borax' is at present confined. In the Middle Ages, borax was imported by Europe from Central Asia, Venice being the centre of purification of the crude tincar. In 1702, HOMBERG prepared boric acid (*sel sédatif de Homberg*) by heating borax with ferrous sulphate, and in 1747–8 BARON concluded that borax was a compound of *sel sédatif* and soda, further suggesting that the former was not a salt but an acid. In 1808, DAVY prepared impure boron by heating potassium and boric acid together in a gold tube, and suggested the name *boracium* for it, under the impression that it was metallic. Four years later, however, he realized that it was a non-metal, and altered 'boracium' to 'boron,' by analogy with carbon.

Occurrence and Extraction.—Boron is not a very abundant element. It invariably occurs in the form of borates or related

compounds. The principal deposits are in the Mohave Desert and the Death Valley of California, where there is found the mineral *colemanite*, a calcium borate with the formula $Ca_2B_6O_{11} \cdot 3H_2O$. In Chile and Peru there are deposits of *ulexite*, which has the formula $Na_2Ca_2(B_4O_7)_3 \cdot 18H_2O$. Among the oldest sources of boron compounds are the hot springs of Tuscany, where the steam and hot water issuing from the ground carry with them small quantities of boric acid, H_3BO_3, but these, though still exploited, are now of small commercial importance.

The colemanite or ulexite is crushed to a fine powder and shaken in large wooden vessels with water through which sulphur dioxide is bubbled, or with dilute sulphuric acid. The liquid is then filtered and evaporated by the heat of the sun, when fairly pure boric acid crystallizes out; it can be purified by recrystallization. Alternatively the process may be worked in conjunction with the sodium nitrate industry. One of the by-products of this industry is sodium hydrogen sulphate, and a solution of this substance may be boiled with the finely-crushed ore and water to produce a boric acid solution, which is evaporated in the manner already described. The best qualities of ulexite are exported to Europe, where borax is made from them.

Elementary Boron.—Boron oxide is a very stable compound the reduction of which offers great difficulties. As no practical use has been found for the element, the methods of preparing it have not received much attention, and it is still something of a chemical curiosity. Amorphous boron is obtained by reducing boric oxide, B_2O_3, boron fluoride, BF_3, or potassium fluoborate, KBF_4, with sodium, potassium, or magnesium. The crystalline product prepared by the reduction of boric oxide with aluminium powder is a mixture of aluminium borides. When freed from excess of aluminium by prolonged treatment with hydrochloric acid, amorphous boron results. Boron of 92-per-cent purity can be prepared by the electrolysis of a mixture of boric oxide, magnesium oxide, and magnesium fluoride at 1100° in a charcoal crucible acting as anode. The cathode is made of iron, and the cathode deposit, which consists mostly of boron, is ground up with hydrochloric acid. A purer variety may be prepared by striking high-tension alternating sparks in a mixture of boron trichloride vapour and hydrogen, or by exposing the same mixture to the action of a glowing filament of tantalum. Pure crystalline boron has recently been prepared by the last method. Crystals develop upon the filament, but as the temperature does not fall, they must be non-conducting.

Properties.—On account of the difficulty of preparing the pure element, our knowledge of the properties of boron is not very precise. It is described as forming lustrous, dark-coloured, and

opaque crystals, which appear to belong to the tetragonal system. Its density is about 2·3 and it is hard and very brittle.   Its melting-point is 2200°–2500°, and it is a non-conductor of electricity; in this respect it is sharply distinguished from aluminium and resembles carbon or silicon.   It is unaffected by air, whether dry or moist, at ordinary temperatures, but it burns if strongly heated in air or oxygen.   It will not dissolve in water, but at a red heat it will decompose steam or the oxides of carbon.   Among the halogens, only fluorine attacks the element at ordinary tempera-tures, but boron will combine with all the halogens on heating, and also with sulphur.   When strongly heated in nitrogen or ammonia, boron forms the nitride BN.   Boron will not dissolve in cold dilute acids or alkalis, but the oxidizing acids react with it, and so do fused caustic alkalis; with these the products are hydrogen and a borate.   It will be noticed that in its chemical properties boron resembles carbon more than any other element.

Boron Hydrides.—Our knowledge of these curious substances was originally due to STOCK and his collaborators (1912 onwards).   They
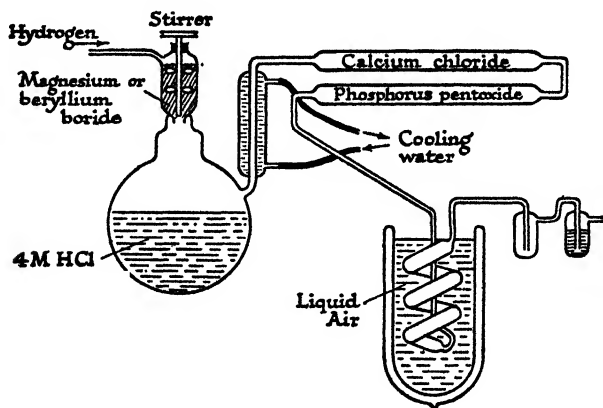
were obtained, in an apparatus similar to that used by the same investigators for the preparation of the hydrides of silicon (Fig. 120), by the action of excess of 4N hydrochloric acid on magnesium boride, which is a mixture of several magnesium-boron compounds. As the mixture of hydrides is spontaneously inflammable, it must be prepared in an atmosphere of hydrogen.   The gaseous products of the reaction, mixed with hydrogen, are dried with calcium chloride and phosphorus pentoxide and passed through a coil cooled with liquid air, in which the hydrides of boron collect as a colourless

liquid consisting almost entirely of *tetraborane*, B_4H_{10}.   After puri-
fication by vacuum distillation at a low temperature, it is found to
freeze at $-112°$ and to boil at $17°$.   It is spontaneously inflammable
in the air, and with water slowly yields boric acid and hydrogen:

$$B_4H_{10}+12H_2O=4H_3BO_3+11H_2\uparrow.$$
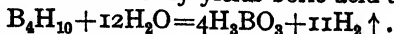
It is unstable, and decomposes into hydrogen and other hydrides
of boron.   At $100°$ this decomposition is rapid, and yields a mixture
of hydrogen, *diborane*, B_2H_6, and other substances.   The mixture
of gases is condensed with liquid air, and diborane can be obtained
from the product by fractional distillation.   In this original pro-
cedure all the diborane and much of the tetraborane that may have
been formed on acidification are lost by reaction with water.
Diborane is obtained in theoretical yield by the following means:
(*a*) lithium hydride (p. 435) reacts with aluminium chloride in ether
solution to give *lithium aluminium hydride*:

$$4LiH+AlCl_3=LiAlH_4+3LiCl,$$
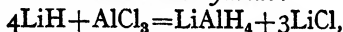
(*b*) on addition of boron trichloride to the solution diborane results
from the reaction:

$$3LiAlH_4+BCl_3=2B_2H_6+3LiCl+3AlCl_3.$$
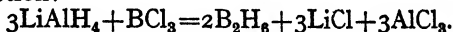
Diborane is the simplest boron hydride, as no other has yet been
prepared with less than two boron atoms in the molecule.   It
melts at $-169°$ and boils at $-87°$, so that at room temperature
it is a gas.   It is not spontaneously inflammable if freed from traces
of the higher hydrides, but it is decomposed by water, yielding,
like the other hydrides, boric acid and hydrogen:

$$B_2H_6+6H_2O=2H_3BO_3+6H_2\uparrow.$$
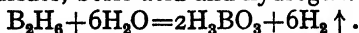
It reacts with the halogens to form first a derivative, such as B_2H_5Br,
which then decomposes according to the equation:

$$6B_2H_5Br=5B_2H_6+2BBr_3.$$
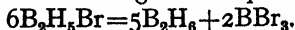
With carbon monoxide or trimethylamine diborane yields respec-
tively the co-ordination compounds $H_3B\leftarrow CO$ and $H_3B\leftarrow N(CH_3)_3$,
which contain the *borine* radical unknown in the free state.

The constitution of diborane and of the other hydrides of boron
is a puzzle of which no complete explanation has yet been ad-
vanced.   Only four of the hydrogen atoms can be replaced to yield
derivatives of diborane, such as $B_2H_2(CH_3)_4$: the remaining two
atoms appear necessary to the structure.   The infra-red absorption
spectrum of diborane is best interpreted by a pattern of atoms
$^H_H{:}B{:}^H_H{:}B{:}^H_H$, and all boranes of known structure contain boron
linked through hydrogen in a similar way.   The detailed nature of
this linking is a still incompletely solved problem.

When diborane is heated to a moderate temperature, say $120°$,
it slowly decomposes, and yields a mixture of solid hydrides.

The most volatile of these has the formula $B_{10}H_{14}$. It is a crystalline substance which melts at 99°, and is distinguished from the lower hydrides by its stability towards water, on which it floats undecomposed. It is decomposed by oxidizing agents.

The Borides.—These compounds are made by union of the elements, or by heating borates or boron oxide with metals, with or without other reducing agents, such as carbon. The high temperature of the electric furnace is sometimes required for these reactions. The borides resemble the carbides and silicides. They are mostly insoluble in water and unaffected by it, but a few, such as the borides of beryllium or magnesium, when treated with water yield a mixture of boron hydrides and hydrogen. Carbon boride, CB_4, vies with the diamond in hardness.

Oxides of Boron.—The only important oxide of boron is the *trioxide*, B_2O_3, though it is said that lower oxides have been obtained by the action of cold water on magnesium boride, i.e. in effect, by the hydrolysis of the boron hydrides.

The trioxide is usually prepared by strongly heating boric acid, H_3BO_3, until no more water is driven off. Commercial boric acid is seldom very pure, but it can be purified without difficulty by several recrystallizations. When obtained in this way the trioxide is a colourless glassy substance and has no melting-point, since it is an undercooled liquid. Its boiling-point has not been precisely determined, but is known to be high. The glass is hard and brittle, but softens on heating.

Boron trioxide dissolves in water to form solutions of boric acid, H_3BO_3, and is a very hygroscopic substance. In moist air it takes up water in two stages, the first yielding metaboric acid, HBO_2, by the reaction:

$$B_2O_3 + H_2O = 2HBO_2,$$
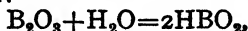
and the second orthoboric acid:

$$HBO_2 + H_2O = H_3BO_3.$$

Boron trioxide is converted to the nitride if strongly heated in ammonia gas, but it resists the action of all the halogens except fluorine, though it reacts with them if strongly heated in their presence with carbon or some other reducing agent. It has already been pointed out that the reduction of boron trioxide to boron is a matter of great difficulty.

Boric Acid.—In addition to *orthoboric acid*, H_3BO_3, both *metaboric acid*, HBO_2, and *tetraboric acid*, $H_2B_4O_7$, are known in the solid state, but in solution they are converted to the ortho-acid. X-ray analysis shows that the metaborates are, e.g., $K_3B_3O_6$, and the existence of the simple acid HBO_2 is doubtful. Borates are known derived from a large number of condensed boric acids, but of the

acids themselves only these three representatives have been certainly isolated.

Some boric acid is derived from the hot springs of Tuscany, but by far the larger proportion of the world's production comes from the borate deposits of North and South America. In the laboratory boric acid is made by adding acids to concentrated solutions of borax (sodium tetraborate), and crystallizing the precipitate from water. Orthoboric acid is a colourless crystalline solid which feels slippery between the fingers. At 100° or a little over it forms the meta-acid, HBO_2, and at 140° the tetra-acid, $H_2B_4O_7$, from which borax is derived.

Boric acid is not very soluble in cold water (about 50 gm. per litre at 15°) but is readily soluble in hot water, so it can easily be purified by recrystallization. In solution it behaves as a very weak monobasic acid of dissociation-constant about 2×10^{-9}. This monobasic behaviour does not indicate any difference in the mode of attachment of the hydrogen atoms in the molecule, but merely a disinclination on the part of any of them to leave it. The acid is soluble in the alcohols, and yields a fairly constant partition-ratio between these solvents and water, indicating a feeble dissociation in the water layer and a uniform molecular condition in both. The feeble acidity of boric acid makes the titration with caustic alkalis difficult, if not impossible, as the hydrogen ion concentration at the equivalence-point is only 10^{-11}. It is, however, found that the addition of glycerol or mannitol to boric acid greatly increases its dissociation, and in the presence of these substances boric acid can be titrated to an end-point in the region $10^{-8}–10^{-9}$ with phenolphthalein. It is supposed that boric acid forms complexes, stronger acids than boric acid, and probably of a chelate nature, with these hydroxylic compounds (compare the effect of glycerol on alumina). Boric acid is too weak to display the usual acidic properties, but its boiling concentrated solutions will liberate carbon dioxide from carbonates.

Boric acid (sometimes called 'boracic acid'), boron trioxide, and borax are all extensively used in the manufacture of glass. The incorporation of these substances in glass raises the refractive index, but litharge is more effective in this respect, and the effect of boron compounds on the thermal properties is more important. The glass is less liable to devitrification at high temperatures and has a low coefficient of expansion, so it is less likely than other kinds to crack on heating, and is used in lamp chimneys and for electric-light bulbs. Jena glass and other types specially made to resist the action of chemicals also contain boric oxide, which increases the resistance to alkalis, though not to acids; it also increases the mechanical strength.

Boric acid is used as a mild disinfectant and for many other purposes. Its use as a preservative of food has been held to be harmful and is now regulated by the law.

Borates.—These salts are derived from a whole series of condensed boric acids.

Borax, sodium tetraborate, $Na_2B_4O_7.10H_2O$, is by far the most important of the borates. It is made on a large scale, chiefly in France and Belgium, from imported colemanite and ulexite, which have been ground and dried in the country of origin. They are first washed to remove chlorides, and are then heated with water, sodium carbonate, and sodium bicarbonate. Calcium carbonate is precipitated, and borax goes into solution; it is precipitated from the filtered liquid on cooling, and is purified by another crystallization.

When borax is heated it loses water and swells into a voluminous spongy form, which on stronger heating is converted to a liquid consisting of the anhydrous salt, $Na_2B_4O_7$. On cooling in the absence of moisture this sets to a transparent glass. Fused borax has the unusual property of dissolving many of the metallic oxides, often with the production of strongly coloured glasses. This is made use of in the 'borax bead' tests of qualitative analysis. Borax (usually the powdered anhydrous salt) is fused in a loop of platinum wire and touched with a little of the substance under examination: from the colour it is often possible to identify the metal. Fused borax is also used, in welding and brazing metals, to dissolve any oxides which may form on the surfaces to be joined.

Like all borates, borax is hydrolysed in solution (more than 2 per cent in M/100 solution), and has a pronounced alkaline reaction. In concentrated solution, with many metallic salts it produces precipitates of borates, but in very dilute solutions the hydrolysis reaches a point at which hydroxides or oxides are precipitated: thus with silver nitrate solutions white silver borate is produced at ordinary dilutions but brown silver oxide in very dilute solutions.

Perborates.—Perboric acid itself has not been isolated, but perborates, derived from the acid HBO_3, are well known. They were first prepared by the treatment of concentrated borate solutions with alkali and hydrogen peroxide, but are now prepared either by anodic oxidation of alkaline borate solutions or by treating borates with sodium peroxide.

Sodium perborate, $NaBO_3.4H_2O$, is prepared on a fairly large scale by electrolysis of solutions of borax and sodium carbonate at a low temperature with a platinum anode. It is a colourless crystalline compound not very soluble in water (about 25 gm. per litre at 15°). The solutions are strong oxidizing agents and

lose oxygen on heating. They have an alkaline reaction, and the perboric acid produced by hydrolysis appears itself to be hydrolysed with the formation of boric acid and hydrogen peroxide, according to the equation:

$$HBO_3 + 2H_2O \rightleftharpoons H_3BO_3 + H_2O_2.$$
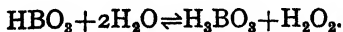
The oxidizing powers of perborate solutions are those of hydrogen peroxide, but sodium perborate has the advantage of being stable in the solid state and easier to transport, while as compared with sodium peroxide it yields a much less strongly alkaline solution. It is accordingly used in disinfectant preparations, in bleaching, and in some well-known soap powders, though it is said to have a destructive effect on clothes.

Boron nitride, BN, is obtained by heating boron to a high temperature with nitrogen or with various nitrogen-containing substances, or more conveniently by strongly heating boric oxide in a stream of ammonia. It is a white powder which, though of amorphous appearance, can be shown by the X-ray method to be crystalline, and to have the crystal structure of graphite (diagram on p. 89). Each boron atom is surrounded by three equidistant nitrogen atoms, and vice versa. This very close-knit crystal structure is in agreement with its chemical inertness. It melts only at a very high temperature (3000°) and is resistant to chemical attack; thus it is insoluble in water and, if it has first been strongly heated, is scarcely affected even by boiling water. It can be ignited in oxygen only at a high temperature, and is only slowly attacked even by hot concentrated acids, with the formation of boric acid and ammonium salts.

BORON HALIDES.—These are colourless compounds which much resemble each other in chemical properties, though the fluoride and, to a less degree, the iodide have some peculiarities. From the list of their melting- and boiling-points it will be seen that at ordinary temperature the fluoride is a gas, the chloride and bromide liquids, and the iodide a solid. In view of the formulae of the

	BF_3	BCl_3	BBr_3	BI_3
Melting-point	−127°	−107°	−46°	43°
Boiling-point	−101°	13°	91°	210°

hydrides of boron, it is interesting to note that the halides have a vapour density corresponding with the simple formula BX_3. They are all hydrolysed by water, the first products being boric acid and hydrogen halide, and all except the iodide consequently fume in moist air. They are purely covalent compounds.

Boron trifluoride, BF_3, is prepared by heating boric oxide with concentrated sulphuric acid and a fluoride, usually cryolite, $AlF_3.3NaF$. It is a colourless gas with a pungent smell, and will

not burn; like all the halides of boron it readily forms additive compounds with ammonia and other donor substances. The compound $BF_3.NH_3$ is a white solid, stable in the absence of moisture; it can be sublimed unchanged.

Boron trifluoride is exceedingly soluble in water. Its concentrated solutions are viscous liquids supposed to contain *fluoboric acid*, HBF_4, formed by the union of boron trifluoride with the hydrogen fluoride produced by hydrolysis, since with bases fluoborates of the metals can be obtained from them. Like hydrofluoric acid, fluoboric acid attacks glass, and must be kept in rubber or wax vessels. Solutions of the acid can be more easily prepared by dissolving boron trioxide in hydrofluoric acid.

The fluoborates are stable compounds which on strong heating yield boron trifluoride and a fluoride of the metal. Fluoboric acid, unlike (oxy-)boric acid, is a strong electrolyte, since solutions of its salts are very little hydrolysed and do not attack glass. They are mostly soluble in water, but *potassium fluoborate*, KBF_4, is only slightly soluble, and is precipitated as a colourless crystalline substance when solutions of the acid are mixed with solutions of potassium salts. The insolubility of this salt is another feature of the strong resemblance between fluoboric and fluosilicic acids.

Boron trichloride, BCl_3, is made by union of the elements, or more easily by passing chlorine over a strongly heated mixture of boric oxide and carbon, and collecting the product in a receiver cooled by a freezing-mixture. The trichloride is purified by fractional distillation. It forms additive compounds with ammonia, phosphine, phosphoryl chloride, nitrosyl chloride, and other substances.

Boron tribromide, BBr_3, resembles the chloride in its methods of preparation and in its properties, though it is much less volatile.

Boron tri-iodide, BI_3, is prepared by strongly heating boron in a current of hydrogen iodide. The product, which distils, is freed from iodine by dissolving it in carbon disulphide and shaking with mercury. Unlike the other halides, it will burn if strongly heated in air or oxygen, liberating iodine and leaving the oxide. The crystals are very hygroscopic and are decomposed by water, but will dissolve unchanged in carbon tetrachloride or benzene.

Boron sulphide, B_2S_3, is obtained by heating boron in hydrogen sulphide, or by heating boric oxide and carbon in the vapour of carbon disulphide. It is a colourless solid which melts at 310° and burns when heated in oxygen. It reacts violently with water, forming hydrogen sulphide and boric acid.

Boron sulphates.—By the interaction of boric and sulphuric acids or their anhydrides, various substances have been prepared which by the action of water yield boric and sulphuric acids. Thus

when boric acid and sulphur trioxide are mixed, and the product is heated to 100°, *boron hydrogen sulphate*, $BH_3(SO_4)_3$, is obtained as a colourless hygroscopic solid melting at 215°:

$$H_3BO_3 + 3SO_3 = BH_3(SO_4)_3.$$
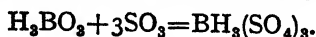
Boron phosphate, BPO_4, is obtained by boiling boric and phosphoric acids together and evaporating to dryness:

$$H_3BO_3 + H_3PO_4 = BPO_4 + 3H_2O \uparrow.$$
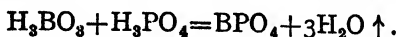
It is a colourless solid with a high melting-point which is insoluble in water and chemically unchanged even by boiling water, but it is decomposed by hot concentrated caustic alkalis.

ALUMINIUM

$Al = 26 \cdot 97$. *Atomic Number*, 13

History.—The word 'alum' is derived from the Latin *alumen*, 'a mineral salt with an astringent taste'—probably crude aluminium sulphate contaminated with various impurities. STAHL (1702) believed the basis of alum to be a distinct calcareous 'earth,' an opinion confirmed by POTT in 1746. MARGGRAF (1754) obtained alumina from clay, and showed that, while an 'earth,' it was not calcareous, but rather like silica. In 1782 LAVOISIER suggested that alumina was a metallic oxide, and in 1824 OERSTED claimed to have isolated metallic aluminium by the action of potassium amalgam on aluminium chloride. Three years later (1827) WÖHLER obtained the metal, in the form of a grey powder, by heating the chloride with metallic potassium.

Occurrence and Extraction.—Of all elements, aluminium is believed to be the third in order of abundance, being preceded only by oxygen and silicon, and is the most abundant of the metals. A large proportion occurs in the form of aluminosilicates, complex and very refractory substances which cannot at present be profitably used for its manufacture. From this point of view the only important ores are *bauxite*, a hydrated oxide, $Al_2O_3.2H_2O$, always associated with ferric oxide and silica, and to a less degree *cryolite*, $3NaF.AlF_3$, found in Greenland, where it is said to be used by the Eskimos for snuff. The principal deposits of bauxite are in the south of France, South America, U.S.A., Ireland, and Hungary.

For the manufacture of aluminium the bauxite must be purified. It is heated with caustic soda solution under pressure, when the aluminium oxide dissolves as an aluminate while the impurities remain undissolved:

$$Al_2O_3 + 2OH' = 2AlO_2' + H_2O.$$
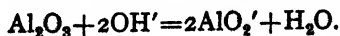
The solution is filtered and pure hydrated aluminium hydroxide precipitated from it either by carbon dioxide or by the addition of a little of the crystalline hydroxide itself. The possibility of carrying out this remarkable process is attributed to the slow spontaneous formation of more condensed and less soluble forms of the hydroxide, the precipitation of which is assisted by seeding with the crystalline substance.

Aluminium, like the alkali-metals, is too electropositive to be made by electrolysis of its aqueous solutions, and is manufactured on a very large scale by the electrolysis of bauxite dissolved in
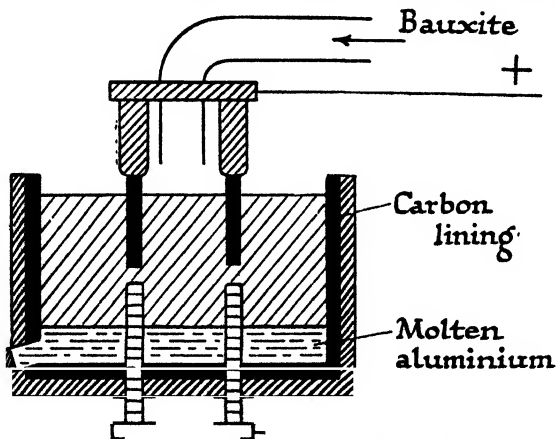
FIG. 121.   MANUFACTURE OF ALUMINIUM

molten cryolite. Since sodium is much more electropositive than aluminium, there is no danger that sodium will be found in the product, but on the other hand any iron present in the bauxite as an impurity will be deposited at the cathode. Pure bauxite must therefore be used. It reaches the aluminium works as a fine white powder that can be forced through pipes like a liquid, and is delivered in this way to the electrolytic furnaces. These furnaces work at 5·5 volts. The anodes consist of carbon blocks, made from gas carbon and pitch pressed together in a mould, and are held in iron sockets. They are slowly attacked by the oxygen evolved at the anode, and last about ten days. The cathodes are made of cast iron. The aluminium alloys with them, and they are periodically removed and sold to iron foundries as ' deoxidizing scrap.' The furnaces are tapped about twice a week; the molten aluminium is run into a bucket conveyor and carried to the refining furnaces as rapidly as possible, since molten aluminium is readily

oxidized by the air. Here it is kept liquid while heavy impurities sink to the bottom as a slag. The oxide is then skimmed from the top and the metal run into moulds. It contains a little iron as impurity.

The manufacture of a kilogram of aluminium by this process requires about 25 kilowatt-hours; a cheap supply of electricity is therefore essential, and to avoid transmission losses aluminium works are usually situated near water-power which can be converted to electricity. The largest aluminium undertaking in the British Isles is the British Aluminium Company at Kinlochleven, in Scotland, where abundant water-power from Ben Nevis is available. These works supplied all the aluminium high-tension cables required by the ' grid ' electricity supply scheme.

The rise of the aluminium industry is one of the romances of industrial chemistry. In 1860, when aluminium was produced by reduction of its compounds with sodium, the metal cost some forty shillings a pound. In 1886 HALL in America introduced the modern electrolytic process, and production increased at such a rate that by 1895 the price per pound had sunk to 1s. 5d. The development of the light aluminium alloys and their modern uses in aircraft, machinery, housing, and metal articles of all kinds has led to a further great expansion in the industry, and production now reaches over 300,000 tons per annum.

Properties.—Aluminium is a silvery-white metal with a density of 2·7. It melts at 659° and boils in the absence of air at about 1800°. The hardness of the metal depends on the treatment to which it has been subjected; at temperatures not far below the melting-point aluminium becomes brittle and may be powdered. It is an excellent conductor of electricity and is now widely used for that purpose in place of the more expensive copper.

In air at ordinary temperatures aluminium becomes coated with a thin film of oxide which tarnishes it. If strongly heated in air or oxygen the metal burns, forming oxide with traces of nitride, and the molten metal is rapidly oxidized in the air. The amalgamated metal is also rapidly oxidized, and a strip of foil treated in this way and exposed to the air soon becomes too hot to hold, while flecks of the oxide appear on its surface. The formation of an oxide film prevents aluminium from dissolving in water, even though its standard electrode potential is about −1·66 volts, but quite small traces of certain impurities either in the aluminium or in the water allow the action to proceed slowly, especially on boiling. The hydrogen ion concentration even of solutions of ammonium salts of strong acids is sufficient to prevent the formation of an oxide film and to allow the dissolution of the metal.

Aluminium dissolves readily in acids if measures are taken to

keep the surface clear. Hydrochloric acid dissolves it under all conditions, but dilute sulphuric acid is nearly without action, as a film, perhaps of hydrogen or perhaps of a basic sulphate, is formed on the surface. This film can be removed by boiling, and the metal liberates hydrogen from hot dilute sulphuric acid, and sulphur dioxide from the hot concentrated acid. In nitric acid of all concentrations the metal readily assumes the passive state, and aluminium containers are used for the transport of this substance.

Aluminium vigorously liberates hydrogen from alkaline solutions. The cause of this reaction is the formation of an aluminate:

$$2Al + 2OH' + 2H_2O = 2AlO_2' + 3H_2 \uparrow.$$
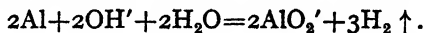
The hydroxyl ion concentration of sodium carbonate solutions is fully sufficient for the reaction to take place.

Aluminium ·is a reactive element that readily unites with all the halogens and can easily be oxidized. Combination with the halogens takes place at room temperature or on gentle heating, and when once started proceeds with incandescence. A dry mixture of aluminium powder and iodine is comparatively stable, but if a drop of water is added it inflames with the production of a purple cloud of iodine vapour. With hydrogen chloride, aluminium produces aluminium chloride and hydrogen even at room temperature.

In the pure state or in alloys aluminium is now used in large quantities for constructional work, cooking utensils, electric cables, aircraft, and in all machinery where lightness and strength are required, e.g. in motor cars. The welding of the metal is difficult on account of the ease with which it oxidizes on heating, and it is usually more satisfactory to replace the damaged part. The two most important alloys of the metal are *duralumin* (about 95 per cent Al, 4 per cent Cu, 0·5 per cent Mg, 0·5 per cent Mn) and *magnalium* (aluminium with 1 or 2 per cent each of magnesium, copper, and nickel). Aluminium is also used as a deoxidizer in the manufacture of steel.

An interesting process has been devised by which aluminium can be coated with a permanent and resistant film of oxide. The article to be coated is made the anode in a bath containing chromic acid. It rapidly becomes covered with an invisible but tenacious coating, and a high voltage is needed to pass the current. Certain dyes can be incorporated in the coating by simply adding them to the bath, and the articles produced in this way can be given a dull polish.

There are several important uses of aluminium powder. The heat of combustion of aluminium is high, some 400,000 calories

per gram-atom, and its great affinity for oxygen has important applications. In a recently invented blowpipe a stream of the powder is burned in a current of oxygen, the resulting temperature exceeding that of the oxy-hydrogen blowpipe. The use of the powder as a reducing agent on the large scale is, however, of much earlier introduction, and is due to GOLDSCHMIDT, whose process for the manufacture of metals whose oxides are difficult to reduce is still in use. In the process this metal oxide is mixed with aluminium powder in a large crucible, usually placed inside another crucible packed with sand in case the first should crack. The mixture is fired by a fuse of aluminium powder and barium peroxide, which becomes incandescent when itself ignited by a burning magnesium ribbon, and starts the main reaction. The heat developed

FIG. 122. GOLDSCHMIDT'S PROCESS

is enough to melt the whole contents of the crucible, and a lump of the metal, often in a state of high purity, collects at the bottom. Thus with chromium the reaction is:

$$2Al + Cr_2O_3 = Al_2O_3 + 2Cr,$$

and the product has a purity of 98 to 99 per cent. Metals prepared in this way are free from carbon, and this is often an important advantage.

A mixture of aluminium powder and ferric oxide is used under the name *thermit* as a source of heat. When once begun the reaction takes place very rapidly, and the temperature produced under favourable conditions is said to exceed that of the electric furnace. Thermit is used for remelting metal in foundries and for welding pipes or rails together; these are simply surrounded by thermit, which is then fired and melts them together.

The explosive *ammonal* consists of ammonium nitrate and aluminium powder. It must be fired by a detonator.

Powdered aluminium is the basis of the so-called 'silver' paint now often used for coating radiators and other metal-work.

Aluminium oxide, Al_2O_3, and hydroxide.—This substance occurs native, not only in the hydrated form as bauxite, but also anhydrous as *corundum*. Many gems, among them sapphires, rubies, and oriental amethysts, consist of aluminium oxide coloured by traces

of oxides of other metals. Artificial rubies have been made by fusing aluminium oxide in the blowpipe with the addition of a little chromic oxide: the product can be distinguished from a natural ruby only by examination under a microscope, which reveals fine bubbles of air in the synthetic material.

The name *alumina* is given to the oxide. Its preparation on the commercial scale has been briefly described. In the laboratory it may be made by heating pure aluminium sulphate to a high temperature with anhydrous sodium carbonate and washing the sodium sulphate from the cooled product. It is a colourless solid, which can be obtained in the crystalline form, and melts at about 2000°. When strongly heated, the oxide suffers an internal change and is no longer hygroscopic. It is very stable at all temperatures, and must be heated very strongly indeed—e.g. with the oxy-hydrogen blowpipe—before it can be reduced with hydrogen. It dissolves only slowly in acids or alkalis, whether in solution or fused. Under the name of *alundum,* the fused oxide has been used in the manufacture of refractory crucibles. Alumina in a finely divided state is the most popular adsorbent in chromatographic analysis (see T. I. WILLIAMS, *An Introduction to Chromatography,* 1946).

The monohydrate, $Al_2O_3.H_2O$, is known as *diaspore,* the tri-hydrate, $Al_2O_3.3H_2O$, as *gibbsite;* they both occur in nature. By the addition of alkaline solutions to solutions of aluminium salts a gelatinous precipitate is thrown down which consists of the oxide, or hydroxide, associated with varying amounts of water. It must be strongly heated before all the water is expelled. When freshly precipitated it is freely soluble in acids, with the formation of aluminium salts, but after it has been kept for some time it grows insoluble. X-ray examination shows that this change in the solubility is accompanied by a change in the crystal structure. The gel very readily absorbs substances from solution, and these cannot easily be removed by washing. It has been used in water purification: a precipitate of the hydroxide is produced in the water by the addition of alum and lime, and this carries down with it any floating impurities.

Aluminium hydroxide is soluble in solutions of sugar, glycerol, and many other hydroxylic organic compounds, with which it probably forms complexes of a chelate type, and it cannot be precipitated by alkalis from aluminium solutions in which these substances are present in sufficient concentration. It is amphoteric and dissolves in acids to form aluminium salts and in bases to form aluminates:

$$Al^{\cdots} + 3OH' \rightleftharpoons Al(OH)_3 \rightleftharpoons H^{\cdot} + AlO_2' + H_2O.$$
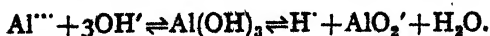
The acidic properties of the hydroxide are very weak, and the

aluminates are much hydrolysed. Most of the available evidence points to a formula AlO_2' for the aluminate ion, and each gram-molecule of sodium or potassium hydroxide will bring approximately one gram-molecule of aluminium hydroxide into solution, in accordance with the equation:

$$Al(OH)_3 + OH' = AlO_2' + 2H_2O.$$
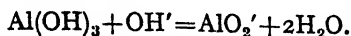
But the aluminates can exist only in alkaline solutions, as otherwise aluminium hydroxide is precipitated, and even carbon dioxide reduces the hydroxyl ion concentration of the solution enough to bring this about.

In the solid state the aluminates of the alkali-metals can be prepared by fusing aluminium oxide with caustic alkali, or by vacuum evaporation of the solutions obtained either in the manner already described, or by dissolving aluminium in aqueous caustic alkalis. They are colourless solids with formulae such as $NaAlO_2$, and various hydrates can be prepared. The hydrolysis of aluminate solutions is a slow reaction, and is also complicated by the molecular change in the hydroxide which has already been alluded to.

In several so-called aluminates, e.g. spinel, $MgAl_2O_4$, there is a lattice composed of the simple ions $Mg^{..}$, $Al^{...}$, and $O^{..}$.

Aluminium peroxide.—By the action of hydrogen peroxide on aluminate solutions a colourless precipitate is produced which has oxidizing properties, and which in addition to aluminium sesquioxide and water is believed to contain an aluminium peroxide, Al_2O_4.

Aluminium nitride, AlN, is prepared by heating aluminium to 800° or over in nitrogen, or a mixture of alumina and carbon may be substituted for the metal. It is a yellow crystalline substance which melts with some decomposition at 2200°; it will not conduct electricity. It is unaffected by hydrogen and must be strongly heated in oxygen or air before any action takes place. With water it yields alumina and ammonia:

$$AlN + 3H_2O = Al(OH)_3 + NH_3,$$
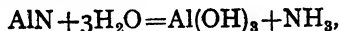
and the manufacture of ammonia from bauxite, coke, and nitrogen was the basis of the now obsolete SERPEK process for nitrogen fixation. The pure alumina produced was used in the manufacture of aluminium.

Aluminium carbonate.—As might be expected, the addition of carbonate solutions to solutions of aluminium salts precipitates not the carbonate, which is unknown, but the insoluble and weakly basic hydroxide.

ALUMINIUM HALIDES.—All these compounds can be made by union of the elements. The conflicting tendencies of aluminium to form electrovalent and covalent compounds are well brought

s

out in this series of compounds, for while the fluoride has a high melting-point and is unaffected by water, the other halides are

	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
Melting-point	1040°	Sublimes at about 183°	98°	91°
Boiling-point			270°	385°

comparatively volatile substances easily hydrolysed. Like other elements, aluminium most readily forms complex ions with the fluorides, and it is interesting to note that whereas the fluoborate ion is BF_4', the fluoaluminate is AlF_6'''; this is a confirmation of the known rule of the covalency maximum. All the aluminium halides readily form addition compounds with donor substances. The fluoride is unaffected by heating in air, while the iodide burns and the chloride and bromide show an intermediate behaviour. Solutions of all the halides except the fluoride have a considerable conductivity from hydrolysis, but the halide molecules appear not to be greatly dissociated, and their covalent character is further shown by their solubility in such solvents as benzene or carbon disulphide.

Aluminium fluoride, AlF_3, is usually prepared by heating aluminium sulphate with sodium fluoride and extracting the product with water. It is a colourless solid, chemically inert and unaffected by acids and alkalis, but hydrolysed by heating in steam. A number of hydrates have been described, some soluble in water and some insoluble. The *fluoaluminates* are obtained by the addition of fluorides to aluminium fluoride. The fluoaluminates of the alkali-metals or ammonium are only slightly soluble in water, and *sodium fluoaluminate*, Na_3AlF_6, which occurs in Greenland as the mineral *cryolite*, is of commercial importance. It is precipitated when sodium solutions are added to a solution of aluminium hydroxide in excess of hydrofluoric acid, and is a stable crystalline substance melting at about 1000° and almost insoluble in water.

Aluminium chloride, $AlCl_3$, is a compound of some importance in the laboratory on account of its use in organic syntheses. Before metallic aluminium was available in quantity, the chloride was usually prepared by the method invented by Oersted, and still much used for the preparation of the chlorides of those metals, such as zirconium, which cannot easily be procured in the elementary state. In this method a mixture of the oxide with carbon is strongly heated in a current of chlorine:

$$Al_2O_3 + 3C + 3Cl_2 = 3CO + 2AlCl_3.$$
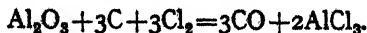
It is now more usual to pass hydrogen chloride or chlorine over

the heated metal in an apparatus such as that shown in the diagram. As the product is attacked by water, the stream of gas must be carefully dried, and to avoid excessive exposure to the atmosphere the chloride is usually collected in the bottle in which it is to be kept. A wide tube must be used to prevent blockage. If necessary, the chloride can be purified by sublimation in a current of dry hydrogen or nitrogen.

Aluminium chloride forms colourless and very deliquescent crystals which sublime on heating, but by rapid heating they can
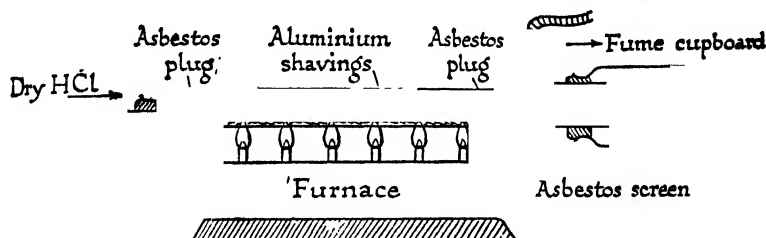
FIG. 123. PREPARATION OF ALUMINIUM CHLORIDE

be converted to a liquid boiling at 183°. The vapour density at temperatures near the boiling-point corresponds with a formula Al_2Cl_6, but at higher temperatures dissociation into simple molecules takes place. In an indifferent solvent such as carbon disulphide, aluminium chloride is polymerized to double molecules, but in donor solvents like water, with which it is probably combined, cryoscopic measurements lead to the simple molecular weight.

The constitution of the double molecule is
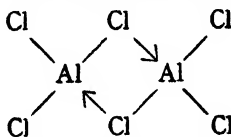
Aluminium chloride is hydrolysed by steam, and when heated in the air yields either an oxide or an oxychloride. It forms addition-compounds with many donor substances, among them ammonia and ammonium salts, phosphine, carbonyl chloride, and certain hydrocarbons such as benzene. The compounds with ammonia are extremely stable, and that with the formula $AlCl_3.NH_3$ has a vapour pressure of only 100 mm. at more than 700°. Aluminium chloride is used as a catalyst in cracking petroleum.

The chloride is extremely soluble in water, and at room temperature (15°) 100 gm. of a saturated solution contain more than 40 gm. of it. The solutions are little dissociated and much

hydrolysed, the hydrolysis reaching nearly 30 per cent in a fiftieth-molar solution at room temperature. The hydrolysis is, however, less than that of ferric chloride solutions in similar circumstances. Evaporation of the aqueous solutions yields the hydroxide mixed with the chloride or perhaps with oxychlorides, but various hydrates of aluminium chloride can be prepared by careful evaporation of its solutions in hydrochloric acid. Unlike the anhydrous salt, these hydrates will not dissolve in such solvents as benzene.

Aluminium bromide, AlBr$_3$, is prepared by the action of bromine vapour on hot aluminium. If liquid bromine is used the action is inconveniently violent, and the heat developed is sufficient to melt the metal. The bromide is purified by distillation, and is a colourless solid resembling the chloride in its properties: like the chloride, it exists in double molecules in the vapour state and in inert solvents. It is easily converted to oxide by heating in the air.

Aluminium iodide, AlI$_3$, is prepared by the action of excess of aluminium on iodine, followed by strong heating to expel any unchanged halogen. The reaction, which is accompanied by incandescence, proceeds spontaneously at room temperature if a drop of water is added to the mixture. The heat developed is then sufficient to volatilize the iodide, which burns in the air with a red flame, forming aluminium oxide and iodine. The iodide is hydrolysed by water.

Aluminium sulphide, Al$_2$S$_3$.—It was a successful attempt to prepare aluminium sulphide by the action of aluminium powder on lead sulphide at a high temperature that led GOLDSCHMIDT to the invention of the process for the reduction of metallic oxides and sulphides which now bears his name. The compound can be prepared by mixing the powdered elements in the correct proportions and starting the reaction with burning magnesium ribbon; combination then takes place with the development of great heat. The sulphide can be purified by sublimation at a very high temperature (1500°) in an inert atmosphere. It is a colourless solid melting at 1100°, and is decomposed by water, so that it cannot be precipitated from aluminium solutions, which are unaffected by hydrogen sulphide and precipitate aluminium hydroxide when treated with ammonium sulphide. The action with water, which takes place according to the equation:

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 \downarrow + 3H_2S \uparrow,$$
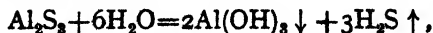
has been used for the preparation of pure hydrogen sulphide. Not all the sulphides of weak insoluble bases are decomposed by water; for this reaction to take place it is essential that the sulphide should be slightly soluble.

Aluminium sulphate, Al$_2$(SO$_4$)$_3$, is prepared on the large scale

from bauxite by dissolving in sulphuric acid the pure hydrated aluminium oxide which can be obtained from this mineral. Numerous hydrates are known, of which the most important is the substance $Al_2(SO_4)_3.18H_2O$, which separates from the aqueous solutions. The sulphate is very soluble in water. If strongly heated, e.g. to 750°, the sulphate loses sulphur trioxide and leaves the oxide.

Aluminium sulphate is used in sizing paper, tanning leather, waterproofing cloth, and as a mordant in dyeing wool or cotton. For these purposes the *alums* are also frequently employed. The alums are double sulphates such as $K_2SO_4.Al_2(SO_4)_3.24H_2O$, a salt to which the name *potassium alum*, or simply *alum*, is given. The univalent metal can be any of the alkali-metals, ammonium, or thallium, and the tervalent metal aluminium, gallium, indium, titanium, vanadium, chromium, manganese, iron, cobalt, rhodium, or iridium, while the sulphur can be replaced by selenium. For a substance to be called an alum, it need not necessarily contain aluminium. The alums are double salts, and in their solutions are decomposed into their constituent ions without any apparent formation of complexes.

Potassium aluminium sulphate, ' *alum,*' $K_2SO_4.Al_2(SO_4)_3.24H_2O$, is precipitated when mixed concentrated solutions of potassium and aluminium sulphates are cooled. This process is carried out on a commercial scale, and alum is also obtained from a basic sulphate *alunite*, which is found at Civita Vecchia, in Italy, and has been used for centuries as a source of alum. This is heated, crushed, exposed to the air, and extracted with water; alum can then be obtained by concentrating the solution. When strongly heated, alum loses water and falls to a friable mass of the dehydrated double salt, called ' burnt alum.'

One hundred grams of boiling water dissolve about 360 gm. of alum, but little more than one-hundredth part of this weight at 0° C. Alum can therefore very easily be purified by recrystallization. As the absence of iron is important in aluminium compounds which are to be used as mordants, alum is for this purpose often preferred to aluminium sulphate, which is not so easily purified. It is also used in tanning leather.

Aluminium nitrate, $Al(NO_3)_3$, can be prepared in solution by dissolving aluminium hydroxide in nitric acid. By evaporation of the solution in the presence of excess of nitric acid to prevent hydrolysis, the hydrate $Al(NO_3)_3.9H_2O$ is obtained, and others are known. The salt is soluble in alcohol and acetone as well as in water. It readily decomposes on heating, and the anhydrous salt has not yet been prepared.

Aluminium phosphates.—Several of these salts are found native in varying degrees of purity, and they can also be prepared by

precipitation, as they are all insoluble in water. Minerals containing phosphates of aluminium are usually acted on only slowly by acids, and are best brought into solution by first fusing them with sodium carbonate and then adding acid to the cold mixture.

Aluminium silicates and the aluminosilicates.—*China clay*, or *kaolin*, is an impure silicate of aluminium, and complex aluminosilicates of the alkali- and alkaline-earth metals occur in nature: they are called *zeolites*. Similar substances, prepared by fusing china clay with sodium or potassium carbonate and sand, have in recent years attained considerable practical importance under the name of *permutites*, and are further distinguished as sodium permutite, calcium permutite, and so on, according to the nature of the alkali- or alkaline-earth metal which they contain. They are porous substances practically insoluble in water, but with the power of exchanging the cation with that of a salt solution in which they are placed. Thus if a solution of a calcium salt is poured through a layer of sodium permutite, the calcium is replaced by sodium in the solution and itself remains in the permutite:

$$2\text{Na permutite} + \text{Ca}^{\cdot\cdot} \rightleftharpoons 2\text{Na}^{\cdot} + \text{Ca permutite}.$$
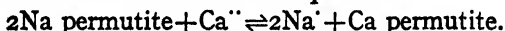
As the reaction is perfectly reversible, the sodium permutite can be recovered by pouring a concentrated solution of brine through the calcium permutite produced. This is the basis of an important process for softening water by removal of the calcium and magnesium salts. Soluble carbonates can also be removed from water by filtration through calcium permutite, which leaves a deposit of calcium carbonate on the permutite.

<center>SUBGROUP A</center>

<center>SCANDIUM, YTTRIUM, LANTHANUM, AND THE RARE EARTH METALS</center>

<center>SCANDIUM</center>

<center>Sc = 44·96. *Atomic Number*, 21</center>

History and Occurrence.—This element was discovered by NILSON in 1879. Its properties were found to correspond closely with those attributed by MENDELEEFF to an element undiscovered at the time of his description of it. Although widely distributed in small quantities, scandium is a scarce element, and usually occurs in association with the rare earths. A mineral *thortveitite* is, however, known that consists essentially of scandium silicate.

For the separation of scandium from the rare earths and thorium special methods have been worked out which cannot be described here. In some processes the element is precipitated as the fluoride, in others as scandium ammonium tartrate, and many further

processes have been devised. Neither scandium nor its compounds are of any commercial importance.

Properties.—In its compounds scandium somewhat resembles beryllium, but it is uniformly tervalent. The hydroxide is a stronger base than aluminium hydroxide, but weaker than the hydroxides of the rare earths. It is distinguished from aluminium hydroxide by its lack of amphoteric properties, as shown by its insolubility in caustic alkaline solutions, but, unlike the hydroxides of the rare earths, can be precipitated by the addition of sodium thiosulphate solutions, which are feebly alkaline through hydrolysis. This is made use of in one process for the separation of scandium from these elements. Scandium hydroxide is not so weak a base that scandium carbonate cannot be precipitated from solution— another distinction from aluminium—but scandium sulphide, like aluminium sulphide, is decomposed by water, at any rate on boiling. The halides of scandium are more salt-like than those of aluminium, they are less hydrolysed in solution, and are much less volatile. All these properties are what would be expected from the position of scandium in the periodic table.

The properties of the metal have not been closely investigated, but 1200° is given as the melting-point.

Scandium fluoride, ScF_3, is prepared by the action of hydrofluoric acid on scandium hydroxide, and much resembles the fluoride of aluminium. It is a very stable substance only slightly soluble in water, but freely soluble in solutions of fluorides, provided that the fluoride ion concentration has not been reduced by the addition of acids. These solutions contain *fluoscandates*, yielding the ion ScF_6''', and stable in the solid state. The complex is fairly stable, since ammonia will not precipitate scandium hydroxide from fluoscandate solutions. The fluoscandates of ammonium and the alkali-metals differ from the fluoaluminate by their much greater solubility in water.

Scandium chloride, $ScCl_3$, is obtained by the action of a mixture of chlorine and sulphur monochloride on hot scandium oxide. It is a colourless solid which melts at 939° and begins to sublime somewhere over 800°, so it is much less volatile than aluminium chloride. Its solutions are less hydrolysed than those of aluminium chloride, and it will not dissolve in alcohol.

Scandium sulphate, $Sc_2(SO_4)_3$, can be obtained in solution by dissolving the hydroxide in dilute sulphuric acid, and crystallizes from these solutions as the hexahydrate $Sc_2(SO_4)_3.6H_2O$, which can be dehydrated by heating. As some hydrolysis takes place, it is best to carry out the heating with a little sulphuric acid.

Scandium carbonate, $Sc_2(CO_3)_3$, can be precipitated from scandium solutions as the hydrate $Sc_2(CO_3)_3.12H_2O$. If this substance is gently heated it loses carbon dioxide as well as water.

THE RARE EARTH ELEMENTS

This term is applied to the elements of atomic numbers 57 to 71 inclusive, as follows:

57 La Lanthanum	62 Sm Samarium	67 Ho Holmium
58 Ce Cerium	63 Eu Europium	68 Er Erbium
59 Pr Praseodymium	64 Gd Gadolinium	69 Tm Thulium
60 Nd Neodymium	65 Tb Terbium	70 Yb Ytterbium
61 Pm Promethium	66 Dy Dysprosium	71 Lu Lutetium

as well as to the remaining members of Group III, Subgroup A, 39, Y, Yttrium, and, more rarely, 21, Sc, Scandium. The two last members of Group IV, Subgroup A, namely, 72, Hf, Hafnium, and 90, Th, Thorium, are also sometimes included, but with less justification. These elements will be considered with the elements of Group IV, and so will cerium, as it possesses features which distinguish it from the rare earths—notably a stable valency of four, feebly marked with praseodymium and neodymium, but unknown in the rest of the group.

The elements of the rare earths are all tervalent, and have similar but not identical properties. They therefore occupy a peculiar position in the periodic table, since most elements are sharply distinguished in properties from their neighbours to the right and left. This peculiarity is reproduced, though more faintly, in the transition elements, and the same explanation has been advanced for both (p. 348), namely that the electron structures of the elements differ not in the valency group but in an inner group. But whereas in the transition elements the variation occurs in the outermost group but one, in the rare-earth elements it occurs in the outermost group but two, and this is why the similarity of properties is so much more strongly developed.

The electron structures assigned to all the elements mentioned are as follows:

Z	Element	Electronic group (p. 346)	IV (18) $(4s, 4p, 3d)$	V (18+14) $(5s, 5p, 4d)$	$4f$	VI (18) $(6s, 6p, 5d)$
21	Sc	(Argon core: I—III, 18)	3	—	—	—
39	Y	(Krypton core: I, II, III, IV, 36)		3	—	—
57	La	(Xenon core: I, II, III, IV, V $(5s, 5p, 4d)$, 54)		—		3
58	Ce		do.		1	3
59	Pr		do.		2	3
60	Nd	Rare-earth	do.		3	3
.	.	elements	.		.	.
.					.	.
71	Lu		do.		14	3
72	Hf		do.		14	4

Throughout the set of rare-earth elements the valency electrons are three in number, two having the type 6s orbit, and one the type 5d orbit. Only in cerium and its next neighbour praseodymium does one 4f electron contribute to a quadrivalency. The xenon core of completed shells is common to them all, so that they differ solely in the content of electrons in 4f orbits.

Occurrence and Extraction.—As their name implies, the rare earths are all scarce elements, though like many other scarce elements they are found in traces in many parts of the world. In practically all rare-earth minerals several elements occur together, and this has added to the difficulty of their investigation.

Gadolinite is a rare earth silicate discovered near Ytterby, in Sweden, by GADOLIN towards the close of the eighteenth century. This obscure northern township has given its name, or parts of it, to no less than four of the chemical elements, namely ytterbium, yttrium, terbium, and erbium. *Samarskite* is a mixed uranate and tantalate of the rare earths discovered in the Urals in 1839, and formerly considered to be a possible source of element No. 85 (eka-caesium, p. 431). The only important modern source of the rare earths is, however, *monazite*, which is essentially a mixture of phosphates of rare-earth metals with about 6 per cent of thorium phosphate. It is worked on the large scale for thorium, and the residues of this process consist of compounds of mixed rare earths from which all requirements can be supplied. For many years no use was known for these substances, and they accumulated in the hands of the manufacturers. Cerium is now an element of some small commercial importance, and the residues are worked for it; but the supply of the associated rare earths considerably exceeds the demand. They are not usually separated from the cerium salts.

Separation of the Rare Earths.—Cerium can be separated without much difficulty from the residues of the manufacture of thorium nitrate, because it is the only member of the rare-earth group to have a stable valency of four. Ceric hydroxide is a feeble base, and the nitrate of quadrivalent cerium is easily hydrolysed to an insoluble basic salt, so that cerium can be separated by boiling the nitrates with excess of water, when the other alkaline-earth nitrates pass into solution. In another method ceric hydroxide is precipitated by permanganate from a solution of a cerous salt:

$$3Ce^{\cdots} + MnO_4' + 10H_2O = 3Ce(OH)_4 \downarrow + MnO_2 \downarrow + 8H^{\cdot}.$$
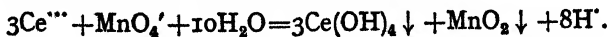
The solution must be kept slightly alkaline by the addition of sodium carbonate. Numerous other methods are available.

The separation of the other rare earths is far more difficult. The first step is usually to divide them into groups according to the

solubility of their sulphates in a cold solution of sodium sulphate. The sulphates of yttrium and the elements of atomic number 65 to 71 (i.e. Tb, Dy, Ho, Er, Tm, Yb, and Lu) dissolve readily, while the sulphates of lanthanum and elements 59 to 64 (i.e. Pr, Nd, Sm, Eu, and Gd) are very much less soluble. The former is called the terbium group, the latter the cerium group, since it is found to include cerium if this element has not already been removed. The elements Sm, Eu, and Gd from the cerium group, and Tb from the terbium group, are sometimes placed in an intermediate group, and if this is done the classification of the rare earths by the solubilities of their double sulphates with sodium leads to the following result:

A. *Almost insoluble:* La, Ce (if present), Pr, Nd.
B. *Slightly soluble:* Sm, Eu, Gd, Tb.
C. *Soluble:* Sc (if present), Y, Dy, Ho, Er, Tm, Yb, Lu.

It is interesting to notice that in the rare earths proper this property follows the sequence of the atomic numbers, while scandium and yttrium come in the same group as lutetium. Many of the properties used in the separation of the rare earths—chiefly solubilities—follow this order or something like it. Measurements of the hydrogen ion concentration of solutions of the rare-earth chlorides show that the order in the electrochemical series is also the order of atomic number (Ce/Ce^{3+}, 2·3 v., Lu/Lu^{3+}, 2·1 v.). In connection with Fajans' theory (p. 340) it may be noted that this order is also the order of decreasing radii of the ions M^{3+} (Ce, 1·18; Lu, 0·99).

Separations within these groups are very difficult, and usually depend either on fractional precipitation of the bases with ammonia, or on fractional crystallization of the salts. The separation of cerium from group A has already been described, and as lanthanum hydroxide is a stronger base than the hydroxides of praseodymium or neodymium, the two latter can be removed by fractional precipitation. An electrolytic method has also been used with success. When solutions of rare-earth salts are electrolysed, the insoluble hydroxides appear at the cathode, the weaker bases predominating in the precipitate. In this way nearly all the praseodymium and neodymium can be precipitated while the lanthanum remains in solution. The separation of these two elements is effected by a laborious process of fractional crystallization from nitric acid of the double nitrates with manganese. From the groups B and C samarium, europium, and ytterbium are separable by reduction since they alone among the rare-earth elements show bivalency.

It is seldom easy to follow in the laboratory the course of a separation, and in the past this has led to much confusion. The determination of the equivalent of the metal present in a sample

is a reliable method, and has been much used when there is a considerable difference between the atomic weights of the rare-earth elements to be separated. It is, however, rather tedious, and when possible resort is had to more rapid methods. Coloured salts, such as those of praseodymium and neodymium, offer obvious opportunities, and measurement of the magnetic susceptibility sometimes provides a useful criterion.

History of the Rare Earths.—An outline of the history of the rare-earth elements has been deferred until this point with the object of giving the reader some idea of the difficulties with which the early workers had to deal. The lack of any rapid or obvious criterion of the individuality of an alleged element led to a large number of claims, nearly all of them now discredited, that new ones had been discovered. MELLOR, in his *Comprehensive Treatise*, gives a list of no less than seventy reported discoveries, most of them unconfirmed. So baffling was the confusion in this field of research that CROOKES at one time suggested that the rare-earth elements were really different forms of the same element. Fortunately in our own day the determination of the atomic number from the X-ray spectrum allows us to state with certainty the permissible number of rare-earth elements and to assign places to those of which specimens are available.

The history of the group begins in 1794 with Gadolin's analysis of the mineral from Ytterby. By 1842, the earth derived from it had been separated into the three earths, yttria, erbia, and terbia. In 1803, cerium was discovered, and in 1842 it was shown to include not only a new earth, lanthana, but also didymia, now known to consist of a mixture of praseodymia and neodymia, but then regarded as a true element. Research continued actively throughout the second half of the century, and was greatly stimulated by the invention of the incandescent gas-mantle, which not only created a demand for thorium and small quantities of cerium, but gave investigators access to abundant supplies of rare-earth compounds produced as by-products of the industry. WELSBACH himself took a prominent part in the discovery of new elements. The last of the rare-earth elements, No. 61, has not yet been confirmed from 'natural' sources. A radioactive isotope, of this atomic number and mass number 145 has however been isolated from the fission products of uranium, and named *promethium* (Pm).

Properties of the Rare-earth Elements and their Compounds.— Only a few of the rare-earth elements have hitherto been isolated, but where the isolation has been accomplished it is either by electrolysing the fused chlorides or by reducing them with alkali-metals. They are grey metals with a density of from 6 to 8. The hardness varies widely from metal to metal, and the atomic volumes,

so far as they are known, lie between 19 and 23. The melting-points are as follows, the differences in the reported results being chiefly due to impurity of the material:

Yttrium	*Lanthanum*	*Praseodymium*	*Neodymium*	*Samarium*
1250°–1490°	810°–826°	940°	840°	1300°–1400°

The metals tarnish in the air, and when ignited burn with a light more intense than that of burning magnesium, forming a mixture of oxide and nitride. They also react when heated in hydrogen, forming brittle hydrides. They are strongly electropositive, and liberate hydrogen slowly from cold water but more rapidly from hot water or dilute acids.

The oxides, with the exceptions noted below, have formulae such as La_2O_3, and are obtained by heating the hydroxides, easily precipitated by caustic alkalis from rare-earth solutions. These hydroxides are only slightly soluble in water and are fairly strong bases, stronger than aluminium hydroxide and of the same order of strength as ammonia. They show no amphoteric properties, and will not dissolve in alkaline solutions. Solutions of rare-earth salts are slightly hydrolysed, but less so than those of aluminium, and the carbonates, unlike aluminium carbonate, can be precipitated in aqueous solution, but the sulphides are decomposed by water, so the addition of soluble sulphides to rare-earth solutions precipitates the hydroxides. The oxides have very high melting-points, and are difficult to reduce; like the hydroxides, they dissolve in acids. The table shows the colours of the oxides and salts of the rare-earth elements having coloured tervalent compounds. Some of the bivalent compounds are also coloured.

	Praseodymium	*Neodymium*	*Samarium*	*Europium*
Oxide	green	blue	pale yellow	pink
Salts	blue-green	pink	pale yellow	yellow

	Dysprosium	*Holmium*	*Erbium*	*Thulium*
Oxide	white	yellow	rose	pale green
Salts	yellow-green	yellow or orange	rose	green

A few of the rare-earth elements display valencies other than three, but the compounds so formed are never very stable. Apart from cerium, which is discussed elsewhere and excluded from this section, praseodymium, neodymium, and terbium form higher oxides when the trioxides are gently heated in air or oxygen. These higher oxides all yield the trioxide and oxygen when strongly heated.

The trichlorides of yttrium, samarium, and europium can be reduced to dichlorides by heating in hydrogen. These dichlorides

dissolve in water to form solutions which are oxidized by the air on boiling, and solutions of samarium dichloride liberate hydrogen even in the cold. Bivalent salts of ytterbium are also known, and europium or ytterbium can be separated as the insoluble bivalent sulphates prepared by electrolytic reduction.

The valency of the rare-earth elements was at one time a matter of controversy, since no compounds are known which are sufficiently volatile to be used in vapour-density determinations. Even to-day the equivalents of many of them, on account of the difficulties of preparing pure material, are known with no great degree of precision, but the order of the atomic weights, and hence the valency, can be deduced with some certainty, either with the help of the X-ray spectrum or by the other methods available (p. 66).

Carbonates.—The hydroxides are sufficiently basic to absorb carbon dioxide, but the carbonates are more easily prepared by precipitating a rare-earth salt solution with sodium hydrogen carbonate. Solutions of normal carbonates precipitate basic salts. The carbonates are insoluble in water, but dissolve in cold concentrated solutions of other carbonates.

Halides.—The *fluorides* resemble aluminium or scandium fluorides in being insoluble in water, though hydrates of some of them have been prepared. They can therefore be obtained by precipitating rare-earth salt solutions with soluble fluorides. They are not hydrolysed even on evaporation to dryness from aqueous solution.

The *chlorides* are much more saltlike and less volatile than aluminium chloride, and consequently cannot be prepared by the action of chlorine on the oxide and carbon. They can be obtained by the action of chlorine or hydrogen chloride on the metal, or more conveniently by dissolving the oxide, hydroxide, or carbonate in hydrochloric acid and evaporating to dryness in a stream of hydrogen chloride to prevent hydrolysis. They are hygroscopic solids soluble in water or alcohol. Their aqueous solutions are slightly hydrolysed, but less so than those of aluminium chloride. Their melting-points, so far as they are known, are as follows (degrees Centigrade): Y, 624; La, 872; (Ce, 822); Pr, 823; Nd, 761; Sm, 682; Gd, 628; Tb, 588; Ds, 680; Ho, 696.

Sulphides.—These compounds have formulae such as La_2S_3; they are decomposed by water, and must be prepared in the dry way, usually by the action of carbon disulphide vapour on the heated oxide.

Sulphates.—These have formulae such as $La_2(SO_4)_3$, and can be prepared in solution by the usual methods. Evaporation of the solutions yields hydrates from which the water of crystallization can be removed by careful heating, an operation which produces a basic salt when applied to hydrated aluminium sulphate. The solubility of the sulphates of all the rare-earth elements decreases

rapidly with rising temperature: thus 100 gm. of a saturated solution of praseodymium sulphate contains 16·5 gm. of the anhydrous salt at 0°, but only 1 gm. at 95°.

Nitrates.—Salts such as $La(NO_3)_3$ can be prepared in solution by the usual methods, and separated from the solution as hydrates, but attempts to prepare the anhydrous salts by heating the hydrates lead to decomposition. The hydrates are soluble in water, alcohol, and acetone.

SUBGROUP B

GALLIUM, INDIUM, THALLIUM

GALLIUM

Ga=69·72.   *Atomic Number*, 31

A comparison of the spectrum of indium, which had been discovered in 1863, with that of aluminium, led the French chemist LECOQ DE BOISBAUDRAN to suppose that an element as yet undiscovered existed with intermediate properties. In 1868 his search was rewarded by the discovery of a new element in a sample of zinc blende from the Pyrenees: he called it gallium in honour of his country. The properties of the new element were substantially the same as those assigned by Mendeleeff to eka-aluminium.

Occurrence and Properties.—Gallium is one of the scarcest of elements, and our knowledge of the metal and its compounds is still imperfect. It usually occurs in minute quantities in zinc blende, and is best separated from zinc, which it somewhat resembles, by electrolysis of an aqueous solution of its salts. Its standard electrode potential lies somewhere between that of zinc, −0·76 volts, and of indium, −0·35 volts, and it can readily be separated by the electrolytic process from aluminium, a metal which cannot be precipitated from aqueous solutions. Alternatively it may be freed from zinc by precipitating the latter as carbonate. Gallium carbonate cannot be precipitated from solution, but the conditions must be carefully controlled, or the hydroxide is thrown down.

The metal obtained by electrolysis is a brittle grey substance with a density of 5·9 and the remarkably low melting-point of 30°. It boils at 2000°. The electrical conductivity is about twice that of mercury, but much less than that of aluminium. Gallium does not tarnish in air, and is stable in air or oxygen unless strongly heated, nor is it affected by air-free water. It dissolves slowly in acids, and will also liberate hydrogen from alkaline solutions.

In its compounds gallium displays a stable valency of three and an unstable valency of one. Gallic hydroxide appears to be a

rather stronger base than aluminium hydroxide, but it is ampho-teric, and gallic salts are partially hydrolysed in solution. They are colourless.

Oxides and hydroxides.—*Gallic oxide*, Ga_2O_3, can be obtained by ignition of the nitrate, or by heating the metal with nitric acid. It is a colourless solid with a high melting-point, soluble in acids or alkalis, but only slowly if it has been strongly heated. The *hydroxide* is thrown down by the addition of caustic alkalis or of carbonates to solutions of gallic salts, which are, however, unlike aluminium salts, unaffected by the addition of soluble sulphides. *Gallous oxide*, GaO, has not been obtained. No **carbonate** of gallium is known.

Halides.—*Gallic chloride*, $GaCl_3$, is prepared by union of the elements. It is a colourless, hygroscopic solid, melting at 76° and boiling at 215°, soluble in water or benzene. It is partially hydro-lysed in aqueous solution or in moist air, and when acted on by excess of water precipitates an oxychloride, GaOCl. The vapour density indicates the existence of double molecules in the vapour phase, but at high temperatures dissociation takes place into single molecules.

Gallous chloride, $GaCl_2$, is prepared by heating the trichloride with gallium. In solution it can be obtained by dissolving the metal in concentrated hydrochloric acid, but these solutions liberate hydrogen if diluted. The salt melts at 170° and is a powerful reducing agent.

By the use of the physical technique of Raman spectroscopy its constitution has been shown to be $Ga^{\cdot}(GaCl_4)'$, and it hence contains both uni- and tervalent gallium:

Gallic sulphide, Ga_2S_3, cannot be prepared in solution; it has, however, recently been obtained by union of the elements.

Gallic sulphate, $Ga_2(SO_4)_3$, can be obtained as a hydrated salt by the usual methods. It is very soluble in water, and the solutions on boiling deposit a precipitate, either of the hydroxide or of a basic salt, which redissolves on cooling. Gallium can replace aluminium in the alums.

Gallic nitrate, $Ga(NO_3)_3$, can be obtained as a hydrated salt by the usual methods, and can be dehydrated in a dry atmosphere at 40°. When heated it yields the oxide.

<div align="center">INDIUM</div>

<div align="center">In$=$114·82. *Atomic Number*, 49</div>

Occurrence and Properties.—In 1863 REICH and RICHTER, with the help of the spectroscope, discovered a new element in zinc blende from Freiberg. They called it indium after the indigo

colour of conspicuous lines in its spectrum. Indium is a very rare element, but its compounds have been more thoroughly investigated than those of gallium. It usually occurs in small quantities in association with zinc, from which it can be separated by electrolysis, or by precipitating it as the hydroxide $In(OH)_3$ with ammonia, with which zinc forms soluble complexes.

Metallic indium can be prepared by electrolysis, or by reducing the oxide with hydrogen or sodium. It is silver-white, has a density of 7·3, and is so soft that it can be squeezed between the fingers. It melts at 155° and boils at 2100°. Its standard electrode potential is −0·35 volts, and it is less electropositive than gallium or zinc, so that pure indium can be deposited from a solution of the mixed salts of these three metals. The metal does not easily tarnish and is unaffected by water, but if strongly heated in air or oxygen it burns. It dissolves rapidly in acids, but not in alkalis: this again distinguishes it from gallium.

Indium has a stable tervalency and (apparently) lower valencies of two and one: these lower valencies are, however, more conspicuous in indium than in gallium. The compounds of indium somewhat resemble those of zinc and cadmium. The trihydroxide is a stronger base than the hydroxides of aluminium or gallium, and indium salts are not much hydrolysed in solution. They are colourless.

Indium trioxide, In_2O_3, is obtained by burning the metal or by heating the nitrate, carbonate, or hydroxide. It is a pale yellow solid with a high melting-point. The *hydroxide* can be precipitated from solutions of indium salts by caustic alkalis or by ammonia, and can be converted to the oxide at 650°. It has feeble acidic properties and will dissolve in cold caustic potash, to be reprecipitated on boiling, but the hydroxyl ion concentration of aqueous ammonia is insufficient to dissolve it. Reduction of the trioxide by hydrogen at a temperature not above 400° leads to a product from which the oxide In_2O sublimes on heating in vacuo at 750°. The existence of an oxide InO is unproved.

Indium carbonate can be precipitated from indium solutions by soluble carbonates: this distinguishes indium from aluminium or gallium.

Halides.—*Indium fluoride*, $InF_3.3H_2O$, is soluble in water, and can be prepared by evaporation of the solution of the hydroxide in hydrofluoric acid. The solutions are decomposed by boiling, and the salt is efflorescent in air. The water can be removed by careful heating at 100°. Indium fluoride is insoluble in alcohol. It can be reduced to the metal by heating in hydrogen.

Indium trichloride, $InCl_3$, is usually prepared by passing chlorine over a heated mixture of the trioxide with carbon. It is a colourless

deliquescent solid, soluble in water and benzene, and volatilizes at about 600°. The vapour density indicates single molecules in the vapour, with a tendency to dissociate, perhaps into the dichloride and chlorine, at high temperatures.

Indium dichloride, $InCl_2$, is a colourless crystalline substance obtained by heating the metal in a current of dry hydrogen chloride. It is decomposed by water into indium and a tervalent salt:

$$3InCl_2 = In \downarrow + 2InCl_3.$$
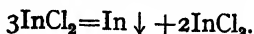
In the light of the recent investigation of gallium dichloride (p. 549) it becomes doubtful whether $InCl_2$ is a correct molecular formula.

Indium monochloride, InCl, has been prepared by distilling a mixture of the dichloride and indium in a current of carbon dioxide. It is a dark red solid whose decomposition by water resembles that of the dichloride:

$$3InCl = 2In \downarrow + InCl_3.$$
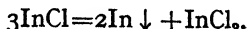
The vapour appears to consist of single molecules.

Indium tribromide, $InBr_3$, obtained by union of the elements, recalls the halides of the adjacent element cadmium in its tendency to form auto-complexes in solution, as shown by conductivity measurements. All the trihalides of indium readily form such complex anions as $InCl_4'$ or $InBr_6'''$, in which the indium has a covalency of four or six.

Indium trisulphide, In_2S_3, unlike the sulphides of aluminium and gallium, can be precipitated from indium salt solutions by hydrogen sulphide, provided the solution is no more than faintly acid. It then appears as a yellow solid soluble in acids, and can be reduced by heating in hydrogen to *indium monosulphide*, In_2S. A red form of the trisulphide is obtained by heating indium with sulphur.

Indium sulphate, $In_2(SO_4)_3$, can be obtained as a hydrated salt by the usual methods, but attempts to dehydrate it by heating lead to the production of a basic salt. The anhydrous *nitrate*, $In(NO_3)_3$, is likewise unknown, as the hydrated nitrate, if heated to a temperature sufficiently high to drive off all the water, yields the trioxide.

<div align="center">THALLIUM</div>

<div align="center">Tl = 204·39.   *Atomic Number*, 81</div>

Occurrence and Properties.—In 1861 CROOKES discovered a new element in the flue dust of a German sulphuric acid works. It was distinguished by a bright green line in the spectrum, and in allusion to this line he gave it the name of thallium (Greek *thallos*, a young shoot).

Though much more abundant than the other members of the subgroup, thallium is a scarce element. As no important uses have been discovered for thallium or its compounds, the extraction of the element from its ores is unprofitable, and the only two considerable sources of thallium are the residues of the lead-chamber sulphuric acid process and the mother liquors of the manufacture of zinc sulphate. The thallium can be separated without difficulty by precipitation as the very slightly soluble thallous chloride, TlCl, after first precipitating as sulphides from strongly acid solution lead, bismuth, silver, and any other elements which might be found in the precipitate.

Metallic thallium can easily be obtained by electrolysis of solutions of thallous salts, or by reducing such solutions with zinc. It is a grey metal with a density of 11·9, resembling lead in appearance, and like lead it is bright when freshly cut, but quickly tarnishes in the air. Thallium is softer than lead and melts at 302°; the boiling-point has been given as 1300°, but much higher values have been reported.

When heated in oxygen the metal burns to thallic oxide, Tl_2O_3, and it will combine with the halogens. The standard electrode potential of thallium is —0·34 volts, very near the value for indium. The metal is unaffected by water, but it will decompose steam at a red heat, forming a mixture of thallous and thallic oxides, and it will dissolve, though not very readily, in dilute acids.

In thallium the group valency of three is not very stable, and the thallic compounds are oxidizing agents derived from the rather weakly basic thallic oxide. The oxidation potential of the change $Tl^{\cdots} \rightarrow Tl^{\cdot}$ is +1·25 volts. The thallous compounds, on the other hand, are very stable, and thallous hydroxide is as strong a base as the caustic alkalis. The valency of three predominates, however, in the covalent thallium compounds (compare the adjacent element lead).

Oxides and hydroxides.—*Thallous hydroxide*, TlOH, is soluble in water and cannot therefore be obtained by precipitation. It can conveniently be prepared by mixing equivalent solutions of thallous sulphate and barium hydroxide, and evaporating the filtrate to dryness. It forms yellow crystals fairly soluble in cold and very soluble in hot water, and it also dissolves in alcohol. It can be converted to thallous oxide by heating to 100° in the absence of air. The solutions are strong bases which, like the caustic alkalis, greedily absorb carbon dioxide from the air; some oxidation may also take place. They also resemble the caustic alkalis in attacking glass when hot and concentrated.

Thallous oxide, Tl_2O, is a yellow solid which darkens on heating: it is prepared by heating the hydroxide in the absence of air. If

heated in the air it takes up oxygen to form thallic oxide. Both thallous oxide and hydroxide are soluble in acids.

Thallic oxide, Tl_2O_3, is obtained by the action of oxygen on molten thallium, which becomes incandescent, or by strongly heating thallous nitrate, or by adding hydrogen peroxide to alkaline thallous solutions. It is a black substance which melts at 725° and in the molten state strongly attacks glass. At low temperatures it is the stablest oxide of thallium, but at 700° the dissociation pressure of oxygen reaches 115 mm. It has some oxidizing properties even in the cold. A reddish-brown solid is precipitated from hot concentrated solutions of thallic salts by ammonia or caustic alkalis, or by oxidizing thallous solutions with permanganate. On the other hand, a yellow solid results from the hydrolysis of thallic chloride—conveniently by the dilution of concentrated solutions of thallic chloride with a considerable quantity of water. It was formerly thought that these two apparently distinct solids were different forms of thallic hydroxide, but X-ray diffraction shows them to be each identical with thallic oxide, and the colour difference must be attributed to different fineness of division. Tervalent thallium, like its neighbour mercury, thus forms no stable hydroxide.

Thallates.—If chlorine is passed into a suspension of thallic oxide in aqueous caustic alkalis, a deep red solution is produced which has been said to contain a thallate. No thallates have, however, been isolated, and if they exist at all they must be very unstable.

Thallium peroxide, Tl_3O_5, has been prepared by anodic oxidation of thallous solutions.

Thallous carbonate, Tl_2CO_3, is obtained by passing carbon dioxide into solutions of thallous hydroxide and then crystallizing the product. It is a colourless solid which melts with some decomposition at 273°, and is often used in the preparation of thallous compounds. It is soluble in water, particularly on warming.

Thallic oxide is too weakly basic to form a carbonate.

Halides.—The monohalides of thallium are salt-like compounds with little tendency to covalency. The solubility relations resemble those of the silver or mercurous halides, that is to say, the fluoride is soluble and the chloride, bromide, and iodide increasingly insoluble; moreover thallous fluoride is by far the most volatile of the halides. The melting- and boiling-points of the thallous halides are as follows (degrees Centigrade):

	TlF	*TlCl*	*TlBr*	*TlI*
Melting-point	327	430	456	440
Boiling-point	655	806	815	824

The thallic halides, on the other hand, are partially covalent: they are hydrolysed and can exist only in acid solution, they are soluble in organic solvents, and are decomposed by heating. All the halides of thallium readily form complexes with donor substances such as ammonia.

Thallous fluoride, TlF, can be prepared by the usual methods, and is a colourless crystalline compound very soluble in water. At 20° the solubility is 80 gm. per 100 gm. of water.

Thallous chloride, TlCl, is prepared by precipitating thallous solutions with soluble chlorides. It is a colourless solid which, like silver chloride, is darkened by light. One hundred grams of a saturated solution in water contain 0·21 gm. of thallous chloride at 0°, and 1·80 gm. at 100°. The salt has been much used for investigations of the solubility-product principle.

Thallic chloride, TlCl$_3$, can be prepared in solution by passing chlorine into a suspension of thallous chloride in water. By evaporation, preferably in a vacuum, white crystals of a hydrate are obtained, and the water can be removed from these in a vacuum desiccator or by very cautious heating. Anhydrous thallic chloride melts at 60°–70° at seven or eight atmospheres pressure, but at higher temperatures it decomposes into thallous chloride and chlorine. It is very soluble in water, and is stable in the presence of excess of hydrochloric acid, but the pure dilute solutions precipitate thallic oxide readily. It is also very soluble in organic solvents, and with donor substances such as ether or pyridine readily forms addition compounds. In the solid state it also forms complexes with ammonia, and in aqueous solution with other chlorides.

Other chlorides of thallium have been prepared with empirical formulae TlCl$_2$ and Tl$_2$Cl$_3$, but they are believed to be complex salts such as Tl(TlCl$_4$) and Tl$_3$(TlCl$_6$): the same applies to the bromides and iodides.

Thallous bromide, TlBr, resembles the chloride, but is pale yellow and less soluble in water.

Thallic bromide, TlBr$_3$, has been made in the same way as thallic chloride, but the salt has not yet been prepared anhydrous, as decomposition begins before all the water of crystallization can be removed.

Thallous iodide, TlI, is prepared like the chloride and bromide, and when precipitated from dilute solutions in the cold is yellow, but red and green forms can also be prepared. It is practically insoluble in water.

Thallic iodide, TlI$_3$, is obtained in black crystals by evaporating mixed alcoholic solutions of thallous iodide and iodine.

Thallous sulphide, Tl$_2$S, is prepared by melting the elements

together in suitable proportions, or by precipitating thallous solutions with hydrogen sulphide in alkaline or weakly acid solution. It is a black substance insoluble in water, soluble in acids with evolution of hydrogen sulphide, and easily oxidized to thallous sulphate.

Thallic sulphide, Tl_2S_3, cannot be prepared from hydrogen sulphide and thallic solutions, as this reaction yields thallous sulphide and sulphur. It is a black substance which must be made by heating thallium with excess of sulphur.

Thallous sulphate, Tl_2SO_4, can be prepared by evaporating to dryness solutions prepared by the usual methods. It forms colourless crystals which melt at 632° and are stable unless very strongly heated. It is not very soluble in cold water, but dissolves better in hot water. A very stable thallium hydrogen sulphate, $TlHSO_4$, is also known.

Thallium forms alums in which it plays the part of the univalent metal, but it cannot, so far as is known, replace the tervalent metal.

Thallic sulphate, $Tl_2(SO_4)_3$, is made by dissolving thallic oxide in sulphuric acid, or by adding barium peroxide to a solution of thallous sulphate.

Thallous nitrate, $TlNO_3$, is made by dissolving thallium in moderately concentrated nitric acid and evaporating the solution to dryness. The product contains some thallic nitrate from which it can be freed by recrystallization. It is a colourless crystalline solid which melts at 206° and on strong heating yields thallic oxide. One hundred grams of water dissolve only 3·91 gm. of the salt at 0°, but 594 gm. at 105°.

Thallic nitrate, $Tl(NO_3)_3$, is obtained by crystallization of a solution of thallic oxide in concentrated nitric acid; the solution deposits thallic oxide if diluted. It is easily decomposed by heating.

Thallous orthophosphate, Tl_3PO_4, is a colourless solid only very slightly soluble in water, and precipitated from thallous solutions by soluble orthophosphates.

CHAPTER XVIII

GROUP IV

CARBON, SILICON, TITANIUM, ZIRCONIUM, CERIUM, HAFNIUM,
THORIUM, GERMANIUM, TIN, AND LEAD

```
                Si
               /  \
             Ti    Ge
             |      |
             Zr    Sn
            /  \    |
          Ce   Hf  Pb
            \   /
              Th
```
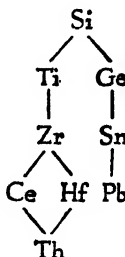
THE table shows some fundamental physical properties:

	Typical		Subgroup A					Subgroup B		
	C	Si	Ti	Zr	Ce	Hf	Th	Ge	Sn	Pb
At. No.	6	14	22	40	58	72	90	23	50	82
At. Wt.	12·01	28·09	47·90	91·22	140·13	178·5	232·05	72·6	118·7	207·21
Density	1·58–1·65	2·46	4·5	6·52	7·0	13·3	12·0	5·5	7·2	11·4
At. Vol.	7·3–7·6	11·4	10·9	13·97	20·0	13·4	19·4	13·2	16·5	18·2
M.-point	3570°	1414°	1725°	1857°	635°	2227°	1730°	958°	232°	327°

In Group IV the systematic differences between the subgroups are very slight, and it is even a matter of some difficulty to decide to which subgroup the typical elements, carbon and silicon, show the greatest resemblance. It will be seen from the table that the atomic volumes are of no assistance in making a choice.

The group valency of four is well marked throughout, and is the principal valency of all the elements in the group except lead. The chemistry of these elements, and particularly of carbon, is dominated by their valency group of four electrons, which allows them to form stable compounds with either positive or negative elements (p. 564), e.g. CH_4 and CCl_4. The stability of the dioxide is

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very marked throughout the group. The tendency to form positive ions increases in the usual way with the atomic number, but positive quadrivalent ions, though not unknown, are of infrequent occurrence on account of their high charge and the rather low atomic volumes of the elements concerned. At the opposite ends of the group carbon and silicon do not form positive ions, while thorium, tin, and lead predominate in this form in solution. On the other hand, the tendency to form volatile hydrides (the hydrides of Subgroup A are solids) increases in Subgroup B and the typical elements with decreasing atomic number, that is, from lead to carbon. The occurrence of valencies lower than four increases from silicon to lead, but decreases from titanium to thorium, and this is connected with one of the principal differences between the subgroups, which may be tabulated as follows:

(i) In Subgroup A a stable valency of three sometimes exists together with the group valency four, whereas in Subgroup B the valency three is unknown and the subsidiary valency is two.

(ii) The elements of Subgroup A have high melting-points (*except* cerium); those of Subgroup B (*except* germanium) have low ones.

(iii) The hydrides in Subgroup A are of the metallic type, while those of Subgroup B are gaseous.

(iv) The tetrachlorides of Subgroup B are volatile liquids, whereas those of Subgroup A are solids (*except* titanium tetrachloride. Cerium tetrachloride is not known).

The typical elements, carbon and silicon, are the least metallic elements of the group, and are the only two elements in it which show no sign of forming a positive elementary ion. Their volatile hydrides (very stable in the case of carbon) connect them rather with the B subgroup than the A subgroup, and germanium shows some power of forming compounds of the ' organic ' type, so characteristic of carbon and to a less degree of silicon. On the other hand their very high melting-points connect them with the A subgroup.

CARBON

$C = 12 \cdot 011$ *Atomic Number*, 6

Occurrence.—Carbon is an invariable constituent of living matter, and is also widely distributed among inanimate substances, though the actual proportion of carbon by weight in the crust of the earth and in the atmosphere is very small. *Carbonates* occur

in such minerals as *dolomite*, $CaCO_3.MgCO_3$, and *limestone*, $CaCO_3$, and in sea-water, while carbon dioxide is found in the atmosphere. Oil (petroleum) consists mainly of hydrocarbons (compounds of carbon and hydrogen), and coal is a complex substance of variable composition containing a high percentage of carbon; it is the product of the decomposition of vegetable matter under pressure. Free carbon also occurs in nature in two forms—*diamond* and *graphite.*

DIAMOND.—The diamond is a hard crystalline form of carbon, that occurs in nature in the form of single stones. The principal localities are India, South America, and South Africa, the last being by far the most important and productive. In most cases, diamonds are found in alluvial deposits, but in South Africa they occur chiefly in ' pipes ' or inverted cones of a ' blue ground.' This ' blue ground ' is generally believed to have been thrown up into the characteristic pipes during the volcanic activity that occurred in South Africa during the Cretaceous period; it consists of weathered ' kimberlite,' an olivine rock. The pipes themselves descend to an unknown depth (a shaft at Kimberley has been sunk to 2600 feet without reaching the bottom of the pipe), and do not all contain diamonds.

To extract the diamonds, a shaft is sunk near, but not actually in, the pipe, and horizontal tunnels are then driven into the blue ground. The diamantiferous earth is run on trams to the shaft, where it is raised to the surface in skips; it is then transferred to sealed trucks, which take it to the crushers. Here it is powdered, washed, and concentrated by levigation, which removes the lighter particles. The ' concentrates ' are then washed down a sloping surface of corrugated iron covered with grease. The diamonds adhere to the grease, but the remaining material is carried off in the stream of water.

Natural diamonds vary considerably in size, lustre, colour, and value: as far as the latter point is concerned it is well to remember that the value of diamonds is largely artificial, being maintained by a restriction of output. The largest diamond hitherto discovered was found in the Premier mine, in the Transvaal, in 1905. It is known as the Cullinan diamond, and before cutting it weighed 3026 carots, i.e. over $1\frac{1}{4}$ lb. (1 carat = 0·2054 gm.). Other well-known diamonds are the Koh-i-noor, the Excelsior, the Victoria, the Hope, and the Star of the South. The Hope is of a beautiful blue colour, while the Dresden Green is of an apple-green shade. Most diamonds, however, are colourless. Black diamonds, known as *carbonado* or *bort*, are valueless as jewels, but are used for making glass-cutters, rock-drills, etc., and, when powdered, for cutting and polishing the colourless stones.

For purposes of jewelry, the natural diamonds are cut in such a way that as much internal reflection as possible is caused; this process requires great skill, and many valuable stones have been spoilt through inexpert cutting. There is always bound to be some loss in weight on cutting a stone, of course, but in some cases it is found necessary to cut the stones down severely. Thus the Koh-i-noor ('mountain of light'), which originally weighed 186 carats, had to be cut down to 106 carats.

Origin of the Diamond.—The origin of the diamond in nature is still a matter of controversy, though it seems possible that diamonds may have been formed when carbon crystallized out from solution in molten iron or in a basic silicate magma, under very great pressure. MOISSAN, in 1893, claimed to have obtained small but genuine diamonds by dissolving carbon in molten iron and quickly cooling the crucible by immersion in molten lead. Under these conditions the iron on the outside of the mass solidified while that inside was still liquid; and since iron expands on solidification, enormous pressures were developed in the interior of the mass when it solidified. On dissolving away the iron with hydrochloric acid, a crystalline product remained which contained some graphite. It has been proved by BRIDGMAN that under all pressures below 30,000 kg./sq. cm. and up to at least 2000° graphite is the stable form, but at pressures above this limit diamond ceases to be changed into graphite. It is an interesting fact that diamonds have been found in meteorites, of both the silicate and iron varieties; but it is possible that such meteorites represent fragments of the earth that were shot into space by ancient volcanoes and, after a journey in space, at length returned to it.

Properties.—The diamond has a high refractive index (2·417 for the D line), and is one of the hardest substances. Its specific gravity is 3·52. Unlike 'paste' diamonds, genuine diamonds are transparent to X-rays, a fact of considerable value to the dealer in precious stones. The diamond is extremely stable towards chemical reagents; pure acids have no effect upon it, though it is slowly oxidized to carbon dioxide by a warm mixture of potassium dichromate and sulphuric acid. It is slowly attacked by fused sodium carbonate, forming carbon monoxide:

$$Na_2CO_3 + C = Na_2O + 2CO.$$
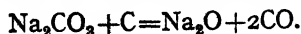
When heated in air to about 800°–900°, it takes fire and burns brilliantly, forming carbon dioxide, and leaving only a minute proportion of siliceous ash.

GRAPHITE.—Graphite is a black, flaky, crystalline substance found in several parts of the earth; most of it comes from Ceylon and the United States. Up to high temperatures and at ordinary

pressures graphite is the stable form of carbon, and at Niagara it is artificially prepared by heating coke in an electric furnace similar to that used for carborundum (p. 566). The charge consists of finely - powdered anthracite, or petroleum coke, to which a little ferric oxide has been added as catalyst. Artificial graphite forms, however, only a small fraction of the total production.

Graphite is used with or without oil as a lubricant, and for polishing metal objects ('blacklead'); it is also used in pencils, and from its power of marking paper the names *blacklead*, *plumbago*, and 'graphite' itself are derived. It is a fair conductor of electricity and is used for electrodes in various technical processes and for the 'carbons' of arc lamps. It is also used in some types of refractory crucible which are to be exposed only to reducing gases, for graphite is attacked by oxygen at 600°–700°.

It has already been shown (p. 89) that the crystal structures of diamond and graphite are in agreement with their observed physical properties.

OTHER FORMS OF CARBON.—These include the various forms of coal, coke, lampblack, soot, wood, and animal charcoal, gas carbon, and sugar carbon. They have generally been described as amorphous, but by the X-ray 'powder' method (p. 87) some of them at least have been shown to be microcrystalline with the graphite crystal structure.

Wood charcoal is a black, very porous substance obtained by burning wood in an insufficient supply of air. Since the affinity of hydrogen for oxygen is much greater than that of carbon, the hydrogen from the carbohydrates burns first and leaves the charcoal behind. Wood charcoal is used as an absorbent for gases, of which it will take up astonishing quantities—sometimes as much as two hundred times its volume at ordinary temperatures and pressures. The lower the temperature the better the absorbing power, and wood charcoal cooled in liquid air is used in perfecting high vacua—a discovery due to SIR JAMES DEWAR which has had much effect on vacuum technique in the laboratory.

Wood charcoal is manufactured on the large scale from peat, a natural product containing carbon chiefly in the form of cellulose. The peat is macerated with phosphoric acid or with a concentrated solution of zinc chloride, and the colloidal solution thus obtained is heated in retorts in the absence of air. A skeleton of wood charcoal remains as a highly porous mass, which is used in gas-masks, for filters, and for 'stripping' benzol from coal-gas.

Animal charcoal is made by heating bones in the absence of air ('destructive distillation'), and consists chiefly of calcium phosphate with about 10 per cent of carbon. It readily absorbs colouring-matters and other substances, and laboratory preparations are

often decolorized by boiling them in solution with animal charcoal. The process is also applied to sugar on the commercial scale.

Soot is a form of carbon deposited when smoke passes over a cold surface.

Lampblack is a very finely divided form of carbon, and though the commercial grades may contain oil and grease as impurities, it can be obtained in a high state of purity. It is manufactured by burning petroleum, naphthalene, the natural gas of oilfields, and other carbonaceous materials, in specially constructed furnaces, the supply of air being limited to the minimum required for combustion. The soot passes along tubes made of sheepskin, canvas, or coarse cloth, whence it is shaken off after the operation is complete. If better qualities are required, the crude lampblack is subjected to a second partial combustion, and the process is repeated as often as necessary.

More than half the world's production of lampblack is used in the motor-tyre industry, since rubber containing 25 per cent of lampblack is about four or five times as resilient and resistant as pure rubber. Much lampblack is also used in the manufacture of printer's ink, while smaller—but still considerable—quantities are employed in making gramophone records, carbon copying-paper, ebonite articles, carbon electrodes, and black pigments.

The application of chimney-soot to garden soil is beneficial because it usually contains up to 7 per cent of ammonia or ammonium compounds, derived from the coal.

Gas carbon remains on the walls of the retorts in which coal is distilled in the manufacture of coke and coal-gas. It is very hard, and is used to make the ' carbons ' of arc lamps.

Sugar carbon is chemically pure carbon obtained by heating sugar until it has charred. In order to remove the last traces of hydrogen and oxygen, it is then heated first in chlorine and then in hydrogen.

PHYSICAL PROPERTIES.—Before discussing the somewhat indefinite substances coal and coke, we may give a comparison of the properties of some carbon allotropes:

	Diamond	*Graphite*	*Gas Carbon*
Density	3·5	2·3	2·2
Transparency	Transparent	Opaque	Opaque
Hardness	Extreme	Soft	Hard
Elec. Conductivity	Non-conductor	Conductor	Conductor
Burns in oxygen at	850°	650°	below 500°

COAL AND COKE.—The coal not consumed in furnaces or domestic fires is subjected to destructive distillation—in the United Kingdom to the extent of about eighteen million tons per annum. The products of the distillation are (i) coal-gas, containing, say, 45 per

cent hydrogen, 35 per cent methane, and 10 per cent carbon monoxide, all by volume, (ii) coke, (iii) tar, (iv) ammonia, and (v) 'benzol,' and the processes may be divided into those which are carried out at 1250°–1400° and those which work at 400°–600°— the so-called 'low-temperature carbonization.' A brief description will be given of the more important of these processes, followed by a summary of the products obtained from them.

High - temperature Carbonization: Coal - gas Manufacture.—The coal is heated in banks of small retorts, which may be either vertical, horizontal, or sloping, at a temperature of between 1250° and 1400°. In the vertical type the process is usually continuous: coal is run in at the top through a sealing device and coke run out at the
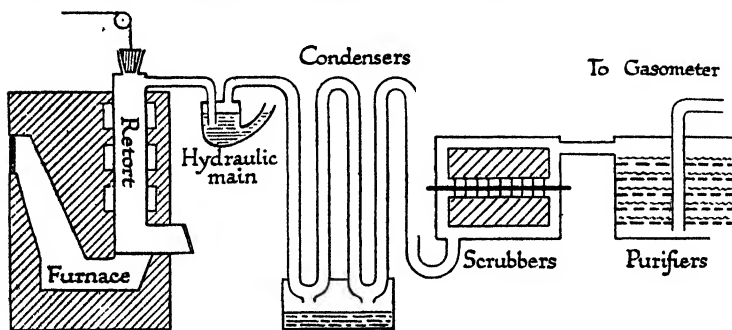
FIG. 124.   COAL-GAS MANUFACTURE

bottom.   In many modern plants steam is blown in at the bottom.   The water-gas so produced (p. 569) increases the volume of gas obtained from a ton of coal, helps to sweep volatile products from the retort, and keeps the temperature down, thereby increasing the yield of tar (which is also more fluid), and the proportion of carbon monoxide and hydrogen in the gas at the expense of the methane.   After leaving the retorts the gases pass through the hydraulic main, a liquid seal which prevents loss of gas when one of the retorts is opened and in which some of the tar is deposited. The gas is then cooled by passing through a series of long pipes, often cooled by water, in which the rest of the tar is deposited, and then passes to the scrubbers, where the ammonia is removed.   In the scrubbers the gas bubbles through water, which by churning is made to offer it a large surface, and in this liquid the ammonia is dissolved.   Before the introduction of the synthetic ammonia process this was the only important source of ammonia.   The gas still contains impurities such as hydrogen sulphide, hydrogen cyanide, carbon disulphide, and carbon dioxide, which must be

removed from it. This operation, is carried out in a series of purifiers, in which the gas flows through perforated wooden shelves on which various purifying agents are spread. The substances most commonly used for this purpose are lime and ferric hydroxide, which remove both hydrogen sulphide and hydrogen cyanide, but the chemical changes involved are too complicated to be discussed here. Before the gas is admitted to the gasometers it is nowadays usual to ' strip ' it: that is, to remove the more volatile liquid hydrocarbons, chiefly benzene, C_6H_6, contained in it as vapour. This is done by passing it through a heavy oil in which the vapours dissolve, or through wood charcoal prepared from peat in the way already described, in which the hydrocarbons are absorbed and from which they can be recovered by heating with steam. These hydrocarbons are known as ' benzol,' and are purified, mixed with petrol, and sold as ' benzol mixture ' motor spirit. It is estimated that twenty-five million gallons of benzol are produced annually in France, and in this country the process is also gaining ground. The illuminating powers of coal-gas are chiefly due to the benzene vapour in it, and if the benzene is removed much of the illuminating power is lost, but this is nowadays of little importance. It is the heating power of gas which determines its value, that is, the heat which can be obtained by the complete combustion of a cubic foot of the gas; this is now the basis of the charge to consumers. Town gas may legally contain sulphur only as carbon disulphide.

Coke Ovens.—In the coke oven the principal product is coke for the manufacture of water- or producer-gas, or for metallurgy, and the gas and tar are by-products of less importance. The coke must contain a minimum of volatile matter, and a high temperature is therefore employed. The volatile products have usually been allowed to run to waste, but in modern coke ovens tar, gas, and ammonia are all collected, and considerable quantities of benzol are obtained by ' stripping ' the gas.

Low-temperature Carbonization.—The objects of this process are to produce (1) a smokeless fuel, ' semi-coke,' in which volatile matter has been left to the extent of some 5 or 10 per cent of the weight of the coke, and (2) a tar or oil like petroleum oil from which liquid fuels, for use as motor spirit or otherwise, can be extracted in quantity. In low-temperature carbonization much less gas is produced, though it is of high calorific value (see table, p. 564).

As these processes are now the object of intensive research in this country and elsewhere, it is impossible to give a final account of them. In the PARKER process, one of the most successful, a smokeless fuel called ' coalite ' is left in the retorts and a very fluid tar is obtained with a high content of phenol and nitrogen compounds.

Representative results of the coal carbonization processes are summarized in the table:

Process	Temperature	Gas			Tar
		Cu. ft. per ton of coal	Heating power per cu. ft. gas B.T.U.	Heating power per ton coal B.T.U.	Gallons per ton coal
High-temperature Carbonization:					
Coal-gas Manufacture:					
Horizontal Retorts	1300°–1400°	13,200	560	7,400,000	9
Vertical Retorts	1250°–1300°	15,600	510	8,000,000	11
Coke Ovens	high as possible	8,500	600	5,100,000	4–8
Low-temperature Carbonization	400°–600°	2,000	800–1500	1,600,000–3,000,000	15–22

The tar derived from these processes is distilled and is a principal source of the organic substances used in industry.

Chemistry of the Carbon Compounds.—The carbon atom has the unique property of forming chains and rings which are the skeletons of stable molecular structures. The number of the carbon compounds is for that reason enormously large (nearly a million are known at present), and they are also much more complex than inorganic compounds; for these reasons their study has become a separate branch of science under the title of ' Organic Chemistry.'

The carbon atom is one of the smallest of all atoms, and this, together with the fact that it has four electrons in its valency group, makes it impossible for carbon to exist as an ion; its compounds are almost invariably covalent. The power of forming long chains is attributed partly to the small size of the atom and partly to the nearly equal strength of the positive and negative affinities; thus methane and carbon tetrachloride are both stable substances. The stability of many compounds of carbon is due to the fact that the covalency maximum of carbon is also four, and that decomposition, if it is to occur, cannot be preceded by combination. This is why carbon tetrachloride cannot be hydrolysed, although silicon tetrachloride is decomposed even by cold water; the covalency maximum of silicon is six.

Radicals are known in which carbon may have a valency of two or three, but the valency of four predominates more than in any other member of the group, except perhaps thorium. The monoxide is a stable substance, its electronic structure resembling that of N_2. The dioxide is weakly acidic and has no trace of basic properties.

In the **acidity** of its normal oxide carbon resembles the elements of Subgroup A rather than those of Subgroup B, but the stability of its volatile hydrides connects it with Subgroup B. The volatility of the oxides of carbon sharply distinguishes it from all other elements of the group.

Properties of Carbon.—The physical properties of some forms of carbon have been discussed. Carbon appears to have a higher melting-point, recently fixed at $3570°$, than any other element: next in order are tungsten, $3370°$, and rhenium, $3140°$. On the other hand carbon has an appreciable vapour pressure at $1300°$ or so, for the old carbon filament lamps grew black on the inside of the glass from sublimed carbon.

Carbon is very resistant to chemical reagents. It will burn if heated in air or oxygen, and is attacked by fluorine in the cold, but not by chlorine even at a white heat. The affinity between carbon and oxygen at high temperatures is used in metallurgy and in many industrial operations. Carbon is unaffected by most acids, but charcoal can be oxidized to carbon dioxide by boiling with nitric acid, and graphite is slowly oxidized, by hot nitric acid containing potassium chlorate, to a mixture of substances in which mellitic acid, $C_6(COOH)_6$, can be detected. In the laboratory carbon is frequently used as a reducing agent at high temperatures.

Carbon is insoluble in all known solvents (except molten iron, etc.); such substances as Indian ink or printer's ink are colloidal suspensions.

Carbon hydrides.—Carbon and hydrogen form a very large number of compounds, known as hydrocarbons; their study belongs to organic chemistry. The simplest are methane, CH_4; ethane, C_2H_6; ethylene, C_2H_4; acetylene, C_2H_2; and benzene, C_6H_6.

CARBIDES.—The term *carbide* is usually restricted to the binary compounds between carbon and the metals, which are solid refractory substances; whereas the compounds with the non-metals are usually volatile, though the carbon compounds of phosphorus and silicon are of the carbide type.

There are two principal methods of preparation:

(i) Direct reaction between the metal and carbon, or the metal oxide and carbon, or the metal and an oxide of carbon.

(ii) A special type of carbide, called an *acetylide*, is made by passing acetylene (C_2H_2) through solutions of some metallic salts.

Examples of both methods of formation will be given.

The carbides, which form a very numerous class of compounds, though many are of slight importance, can best be classified according to their action with water:

Action with Water	Example
No action	Acetylides, silicon carbide, iron carbide
Produce acetylene, C_2H_2	Calcium carbide
Produce methane, CH_4	Aluminium carbide, beryllium carbide

Acetylides.—When acetylene is passed through an ammoniacal solution of cuprous chloride, cuprous acetylide, Cu_2C_2, is precipitated as a red powder. It is explosive when dried. Silver acetylide is a white solid precipitated from ammoniacal silver nitrate by acetylene; it is much more violently explosive than the copper compound. Other acetylides are known.

$$2Cu^{\cdot} + C_2H_2 = Cu_2C_2 \downarrow + 2H^{\cdot} \quad \text{and} \quad 2Ag^{\cdot} + C_2H_2 = Ag_2C_2 \downarrow + 2H^{\cdot}.$$
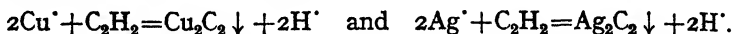
Silicon carbide, SiC, resembles diamond in its inertness. It is prepared on the large scale where electric power is cheap (e.g. in Norway and at Niagara) by heating a mixture of sand (50 per cent) with coke and some sawdust in the electric furnace:

$$3C + SiO_2 = SiC + 2CO \uparrow.$$
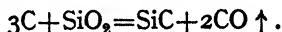
The object of the sawdust is to keep the mass porous and to allow the carbon monoxide to escape; the latter burns on the surface. The heat is provided by the passage of the current through the core of coke and graphite that connects the electrodes, which are set in cement walls at the ends of the furnace. The sides are made of loose bricks which are removed when the reaction is finished. The core is then found to be surrounded by a layer of impure silicon carbide, which is removed and broken up. When pure, it
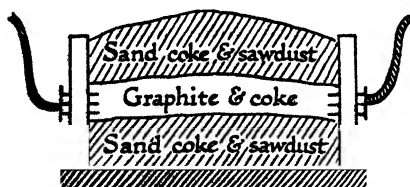
FIG. 125. 'CARBORUNDUM' FURNACE

is a colourless crystalline substance, but the commercial product, e.g. 'Carborundum,' is always coloured. It is nearly as hard as diamond (and has the diamond crystal structure), which makes it very useful as an abrasive. It is also refractory and has been used for crucibles ('Silundum'). Crystalline specimens were formerly used as rectifiers in wireless sets.

Iron carbide.—There are several carbides of iron, of which the most important has the formula Fe_3C. This is a constituent of steel.

Calcium carbide, CaC_2, is made on a very large scale, for use in

acetylene generators, by heating a mixture of coke or anthracite and freshly-burnt lime to a temperature which may reach 3000°:

$$CaO + 3C = CaC_2 + CO \uparrow .$$
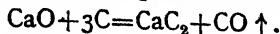
The furnaces are made of iron lined with carbon and are mounted on wheels; they are heated by the passage of an electric current between the bottom of the furnace and a carbon electrode suspended in the top. At the temperature reached, the calcium carbide fuses and sinks to the bottom of the charge, from which it is drawn off at intervals, cooled in trays, and broken up into lumps.

A furnace producing some eight tons of carbide a day will take a current of 30,000 amperes at 50 volts—nearly 2000 h.p.—so the industry can only be established where electric power is cheap. When pure, calcium carbide is colourless and transparent, but the commercial product is grey or black. Calcium carbide is insoluble in all known solvents. It reacts vigorously with water in the cold, producing acetylene, and this is now its principal use:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2 \uparrow .$$
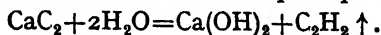
The acetylene can either be generated as is required, or manufactured in quantity and sent out dissolved in acetone under pressure. Since acetylene is now the starting-point of the manufacture of acetaldehyde and other commercially important chemicals, calcium carbide is of considerable industrial importance, quite apart from its use in illumination.

In the laboratory calcium carbide has been used for the estimation of water in organic liquids; the volume of acetylene liberated from a known volume of the liquid is measured. The repulsive smell of the acetylene generated from commercial calcium carbide and water is due to phosphorus hydrides produced from calcium phosphide in the calcium carbide. The phosphorus was originally present as phosphate in the limestone from which the lime was made, and this has been reduced to phosphide in the furnace.

Calcium carbide reacts with nitrogen when heated in the gas to a temperature of 1000° to form *calcium cyanamide* and graphite:

$$CaC_2 + N_2 = CaCN_2 + C.$$
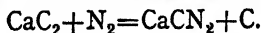
This is the basis of one of the older processes for the fixation of nitrogen (p. 392). The nitrogen is obtained from the air by one of the methods described in connection with the synthetic ammonia process (p. 388), and the calcium carbide is heated either externally or by passing an electric current through it. The mixture produced is called *nitrolim* or *Stickstoffkalk*, and is used as a fertilizer. When it is treated with superheated steam under pressure, ammonia is produced:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3 \uparrow ,$$
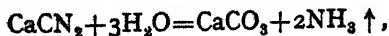
but this process is seriously threatened by the HABER process (p. 388). If fused with sodium chloride, nitrolim yields sodium cyanide, and this process also is worked on a commercial scale:

$$CaCN_2 + C + 2NaCl = 2NaCN + CaCl_2.$$
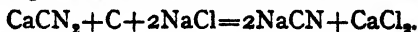
Aluminium carbide, Al_4C_3, is now prepared by heating a mixture of alumina and coke in the electric furnace:

$$2Al_2O_3 + 9C = Al_4C_3 + 6CO \uparrow.$$
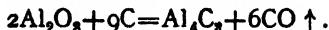
The pure substance forms yellow crystals, but the commercial product is a brown powder, sometimes used in the laboratory for making methane. The action is slow with cold water but becomes vigorous on boiling:

$$Al_4C_3 + 12H_2O = 3CH_4 \uparrow + 4Al(OH)_3.$$
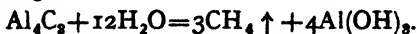
THE OXIDES OF CARBON.—Carbon forms several oxides, of which only two, the monoxide, CO, and the dioxide, CO_2, are important to the student of inorganic chemistry.

Carbon suboxide, C_3O_2, is obtained by removing the elements of water from malonic acid, $CH_2(COOH)_2$, by distillation with phosphorus pentoxide:

$$CH_2(COOH)_2 - 2H_2O = C_3O_2 \uparrow.$$
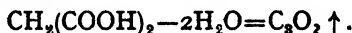
It is also a constituent of the brown powder produced from carbon monoxide by the silent electric discharge. It is a colourless gas with a strong smell, condensing at 6° to a colourless liquid. It burns readily, forming carbon dioxide. With water it yields malonic acid, and is therefore malonic anhydride, but it may also be regarded as a diketene with the structure OC=C=CO.

Mellitic anhydride, $C_{12}O_9$, is a cyclic carbon compound of purely theoretical interest.

Carbon monoxide, CO, is the product of the first stage in the combustion of carbon, and the final product if insufficient oxygen be present. In the laboratory it can be made by heating various carbon-containing compounds with concentrated sulphuric acid, e.g.:

Sodium formate: $H.COONa + H_2SO_4 = NaHSO_4 + H_2O + CO \uparrow.$

Oxalic acid:
$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} = CO_2 \uparrow + CO \uparrow + H_2O.$$
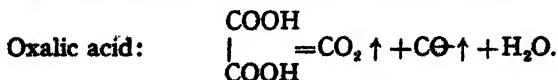
A ferrocyanide: $Fe(CN)_6'''' + 6H_2O + 12H^{\cdot} = Fe^{\cdot\cdot} + 6NH_4^{\cdot} + 6CO \uparrow.$

If oxalic acid is used the gases must be freed from carbon dioxide by bubbling them through caustic potash. The gas can be collected over water, in which it is nearly insoluble.

In industry the gas is produced in very large quantities (and often allowed to escape) in processes in which carbon is used as

a reducing agent; it is present also, to the extent of some 10 per cent by volume, in coal-gas. It is used as a gaseous fuel, and for this purpose is produced by the oxidation of coke either with air (*producer-gas*), steam (*water-gas*), or a mixture of both (*semi-water gas*).

Producer-gas.—The heats of formation of carbon monoxide and dioxide are:

$$2C + O_2 = 2CO + 53,600 \text{ cals.}$$

and $\quad 2C + 2O_2 = 2CO_2 + 188,600$ cals., whence, by subtraction,

$$2CO + O_2 = 2CO_2 + 135,000 \text{ cals.}$$

If no use is made of the heat of formation of the carbon monoxide it follows that of the 94,300 calories obtainable by the complete combustion of a gram-atom of carbon only 67,500 calories, or about 70 per cent, are usefully employed. This loss is generally avoided either by having the producer so close to the furnace where the monoxide is to be burned that the heat is carried by the gas from one plant to the other without much dissipation by the way, or by using the heat from the producer to warm the furnace air-blast, or in some separate process. The producer is filled with coke and started by lighting a fire in it; the air-supply is then so regulated that complete combustion to carbon dioxide cannot take place. Since the gases are continuously withdrawn from the producer no question of equilibrium arises, but the producer must be tall and the temperature must be high (1100° or over) to make sure that any carbon dioxide produced at the bottom shall be reduced to monoxide by the white-hot coke at the top. Producer-gas contains about 65 per cent by volume of nitrogen (and inert gases) from the air, the remainder being carbon monoxide with not more than 2 per cent of the dioxide.

Water-gas.—When coke is heated in steam, hydrogen and carbon monoxide are produced:

$$C + H_2O = CO + H_2 - 30,900 \text{ cals.}$$
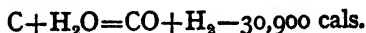
The heat absorbed in the reaction can be calculated from the heats of formation of carbon monoxide and water from their elements, that is, by adding the equations:

$$2C + O_2 = 2CO + 53,600 \text{ cals.,}$$

and $\quad \dfrac{2H_2O = 2H_2 + O_2 - 115,500 \text{ cals.}}{2C + 2H_2O = 2CO + 2H_2 - 61,900 \text{ cals.}}$
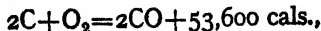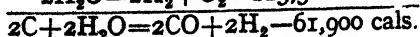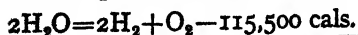
Since the reaction is endothermic, the proportion of carbon monoxide and hydrogen in the gas produced is increased by raising the temperature, but it is found impracticable to supply heat from

outside, so the efficiency of the water-gas production rapidly diminishes as the heat absorbed in the reaction lowers the temperature of the coke. In the older types of plant this was avoided by blowing air at intervals through the whole mass and thereby raising its temperature by the producer-gas reaction, but it is nowadays more usual to carry out these operations simultaneously by blowing in steam mixed with sufficient air to keep the temperature from falling. The product is called *semi-water-gas.* Ordinary water-gas contains (by volume) about 50 per cent hydrogen, 40 per cent or more carbon monoxide, and the rest carbon dioxide and nitrogen, whereas semi-water-gas may contain 50 per cent or more nitrogen, 25 per cent carbon monoxide, and 15 per cent hydrogen, together with some carbon dioxide and methane.

An important modern application of the producer-gas and water-gas processes is to the manufacture of nitrogen and hydrogen. The carbon monoxide is first oxidized to dioxide, which can be removed by dissolving it at high pressure in water. The oxidation is carried out with steam according to the equation:

$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$
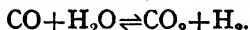
By adding the heat evolved in the reaction:

$$CO + \tfrac{1}{2}O_2 = CO_2 + 68,000 \text{ cals.,}$$

and the reaction:

$$H_2O = H_2 + \tfrac{1}{2}O_2 - 58,000 \text{ cals.,}$$
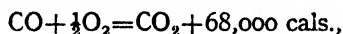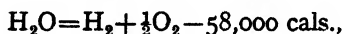
we find that the reaction evolves 10,000 calories when conducted from left to right. The oxidation of the carbon monoxide is therefore favoured by a low temperature, and to secure a reasonable speed at this temperature a preparation of iron or copper is used as a catalyst. The equilibrium is practically independent of the pressure.

Carbon monoxide is a colourless gas whose physical properties resemble those of nitrogen. It is poisonous, and possesses so faint a smell that the victim is frequently overcome without realizing his danger. The toxic properties of coal-gas are due to the carbon monoxide contained in it, and deaths from carbon monoxide poisoning also occur in garages and other confined spaces where motor-car engines are run with an insufficient supply of air, and in unventilated bathrooms with geysers burning. The carbon monoxide combines with the haemoglobin of the blood and prevents it from carrying out its function as the oxygen-carrier of the body. Patients should be removed from the infected atmosphere and given a mixture of oxygen with a little carbon dioxide, which stimulates the lungs and causes panting, thereby helping the absorption of oxygen; but treatment usually comes too late. It may be remarked that, owing to the mechanism of its toxic action, carbon

monoxide does not act as a poison upon those living organisms (e.g. plants) which are bloodless.

Carbon monoxide is nearly insoluble in water. It has the same density as nitrogen, and is therefore very slightly lighter than air. It burns readily in air or oxygen, but only if water-vapour is present. The water-vapour in the atmosphere is sufficient, but a jet of burning carbon monoxide is extinguished if introduced into a wide-necked flask in which the air has been moderately dried by shaking with a little concentrated sulphuric acid. For this experiment the carbon monoxide must first be dried with sulphuric acid, and it must be shown that there is sufficient access of air to the interior of the flask for the gas to burn in it in the absence of a desiccating agent.

Carbon monoxide

Tubes containing pumice and conc. sulphuric acid

Conc. sulphuric acid
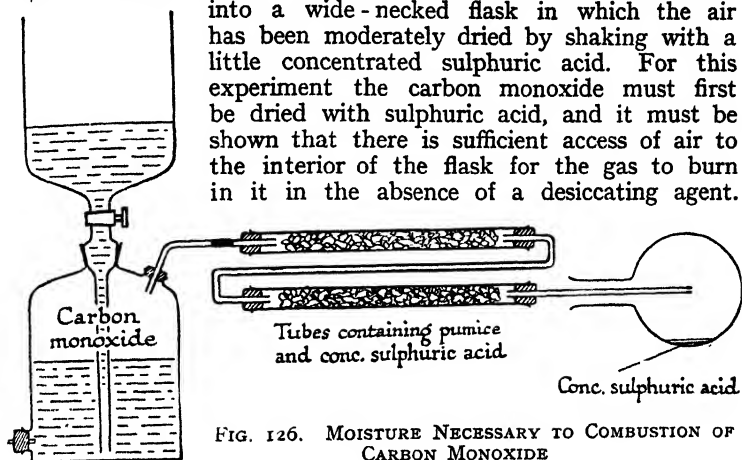
FIG. 126. MOISTURE NECESSARY TO COMBUSTION OF CARBON MONOXIDE

Carbon monoxide is an unsaturated compound, that is to say, it will form addition compounds. This property is, however, far from evident at ordinary temperatures and pressures and in the absence of catalysts and light. Ammoniacal solutions of cuprous chloride absorb it to give a compound $CuCl.CO.H_2O$, but here carbon monoxide is acting as a donor molecule, as in the carbonyls. It will also combine with chlorine, slowly in diffused daylight and rapidly in bright sunlight, to form carbonyl chloride or phosgene:

$$CO + Cl_2 = COCl_2.$$
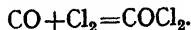
For the remaining addition reactions raised temperatures and pressures or catalysts are necessary. Carbon monoxide will combine rapidly with oxygen at o° C. on the surface of manganese dioxide. With sulphur vapour in a hot tube carbon oxysulphide, COS, is produced:

$$CO + S = COS.$$
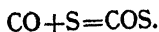
With hydrogen at high pressures and in the presence of a catalyst methyl alcohol can be obtained:

$$CO + 2H_2 = CH_3.OH;$$
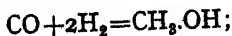
a process which is worked on the industrial scale at 200 atmospheres. With caustic soda in the presence of water at about 200° sodium formate is produced:

$$CO + NaOH = H.COONa;$$
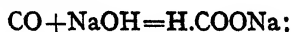
this process is also worked on the commercial scale under increased pressure. At high temperatures the reducing powers of carbon monoxide become more evident, and the gas is widely used in metallurgy for reducing metallic oxides to the metal.

To estimate carbon monoxide in air, its power of reducing iodine pentoxide at a temperature of 70° is employed:

$$I_2O_5 + 5CO = 5CO_2 + I_2.$$
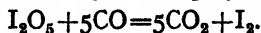
The carbon dioxide produced is swept on by the air stream and absorbed in a solution of barium hydroxide, where it is estimated by titration. The air must first be freed from carbon dioxide.

At moderately high temperatures and usually at high pressures carbon monoxide will react with some of the metals to form *carbonyls* such as iron pentacarbonyl, $Fe(CO)_5$; nickel carbonyl, $Ni(CO)_4$; cobalt carbonyl, $Co_2(CO)_8$. Such carbonyls are formed only by metals of the transitional sequences (p. 771). On strong heating they dissociate into metal and carbon monoxide. Their low boiling-points and solubility in organic liquids point to a covalent structure, e.g.:
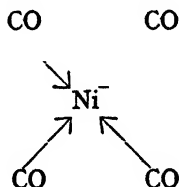
The formation and decomposition of nickel carbonyl is the basis of the important MOND process for the commercial preparation of nickel.

The composition of carbon monoxide is known from the fact that two volumes of the gas, when sparked with one volume of oxygen, produce two volumes of carbon dioxide. Its electronic structure is discussed on p. 339.

Carbon dioxide, CO_2.—*Occurrence.*—Carbon dioxide occurs in the atmosphere to the extent of about 0·03–0·04 per cent by volume, though this proportion varies in different parts of the earth. Large quantities of the gas also issue from volcanoes or other vents in the earth's crust; thus the atmosphere of a certain cave near Naples contains about 70 per cent of carbon dioxide, and the cave is called the Grotto del Cane because the gas forms a layer on

the ground deep enough to asphyxiate any dogs which may venture in. A valley in the Yellowstone Park in California is called Death Gulch for the same reason, and has been described as ' littered with the skeletons of men, animals, and birds.' In Germany natural carbon dioxide issuing from the ground is collected, purified, and sold.

Carbon dioxide is produced by the respiration of animals and plants, but the amount so liberated is an insignificant fraction of the carbon dioxide content of the atmosphere. Of all the gases of the lower atmosphere carbon dioxide most strongly absorbs solar radiation, and it has an important effect on the temperature of the earth, which it reduces. Atmospheric carbon dioxide is the principal food of green plants.

Manufacture.—Carbon dioxide is always present in furnace gases, of which, with nitrogen, it is usually the chief constituent, but it is only seldom recovered from this source, though a process has been developed for recovering it from water- and producer-gas. On the commercial scale it is usually prepared by heating limestone (calcium carbonate), and is therefore a by-product in the preparation of quicklime:

$$CaCO_3 = CaO + CO_2 \uparrow.$$

The furnace in which the operation is carried out is called a lime-kiln; the necessary heat is usually provided by the complete combustion of coke inside the kiln.

For the manufacture of soda- and mineral-waters, which owe their effervescence to carbon dioxide dissolved in them under pressure, a purer gas is required, and this is often obtained from breweries, where it is produced during the process of fermentation. If pure carbon dioxide is to be prepared from furnace gases, these are first passed through water to remove sulphur dioxide, which is much more soluble in water than carbon dioxide is, and are then absorbed in a solution of potassium carbonate, where bicarbonate is produced (sodium carbonate is less suitable, since sodium bicarbonate is not very soluble):

$$CO_3'' + H_2O + CO_2 = 2HCO_3'.$$
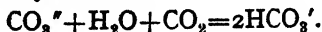
The carbon dioxide is recovered from the solution, which can be used again, by boiling it, when the reverse action takes place. It is dried with concentrated sulphuric acid and sent out in cylinders in which it is confined at a pressure of sixty atmospheres.

In the laboratory carbon dioxide is nearly always made by the action of acids on carbonates:

$$CO_3'' + 2H^{\cdot} = H_2O + CO_2 \uparrow.$$
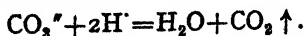
The gas is freed from acid vapour or spray by passing it through a solution of sodium or potassium bicarbonate.

Properties.—Carbon dioxide is a colourless gas, said by some to have a faint but characteristic odour; it certainly produces a tingling sensation on the membrane of the nose when inhaled. It is a heavy gas, twenty-two times as heavy as hydrogen and 50 per cent heavier than air, and since it will not (in general) support combustion, it is used in some types of fire extinguisher, which generate it as required from a carbonate and a dilute acid. The gas keeps low and diffuses only slowly from the burning material, which it deprives of air. The gas was first liquefied in 1823, by FARADAY; at atmospheric pressure the liquid cannot exist, but the solid can do so provided the temperature is below —78°. In the cylinders in which it is supplied at about sixty atmospheres carbon dioxide is a liquid, but on free expansion from such a cylinder so much heat is absorbed that the temperature is reduced below —78° and some solid carbon dioxide, called ' carbon dioxide snow,' forms at the exit tube and may be collected in a flannel bag tied over it during the escape of the gas. A concentrated solution of the solid in acetone, through which air is blown, may reach a temperature as low as —110°. Ether is sometimes used instead of acetone.

The production of solid carbon dioxide is now carried out on a large scale. The gas is first liquefied by pressure, and then solidified by free evaporation. Since at atmospheric pressure the solid turns directly to gas, it leaves no liquid behind it—hence the name ' dry ice.' The latent heat of sublimation (153 calories per gram) is exceptionally high, so that a block evaporates very slowly in still air, being constantly surrounded by an insulating layer of intensely cold gas. It is packed into cartons with ice-cream or perishable goods, and the fact that it disappears without leaving moisture is a great advantage for such purposes. Solid carbon dioxide is also largely used in engineering.

Under atmospheric pressure water dissolves about its own volume of carbon dioxide at room temperature, though the solutions are easily supersaturated. The solution has a feeble but definite acidity. Carbon dioxide deviates in its behaviour from Henry's law. The gas is a feeble poison, but its frequent fatal effects are due rather to the exclusion of air, which causes suffocation, than to any specific effect. The unpleasantness of the air of crowded rooms is due not to carbon dioxide, though its concentration under these circumstances may reach 0·5 per cent, but mainly to the stagnancy of the air in contact with the skin and to the increase in humidity. Immunity to such atmospheres can be attained—if desired—by practice.

Carbon dioxide is a comparatively inert substance. It can be reduced to carbon monoxide at high temperatures by carbon and

some metals, and by magnesium, zinc, or aluminium to carbon; magnesium, if ignited and plunged into the gas, will continue to burn. With ammonia, carbon dioxide combines to form ammonium carbamate:

$$CO_2 + 2NH_3 = NH_2.COONH_4,$$
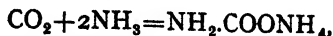
but if water is present beyond the minute quantity necessary to catalyse the reaction, ammonium carbonate is produced. The modern manufacture of synthetic urea depends on the former reaction (p. 390).

Carbonic acid, H_2CO_3, has never been isolated, but it is known to occur in aqueous solutions of carbon dioxide, and its salts, the carbonates, are among the commonest substances of inorganic chemistry. Carbon is not known to form a tetrahydroxide, $C(OH)_4$, but certain organic derivatives of this hypothetical substance are known, such as ethyl orthocarbonate, $C(OC_2H_5)_4$.

In aqueous solutions of carbon dioxide equilibria are set up between carbon dioxide, water, and carbonic acid, and between the acid and its ions:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3. \quad H_2CO_3 \rightleftharpoons H^{\cdot} + HCO_3'. \quad HCO_3' \rightleftharpoons H^{\cdot} + CO_3''.$$
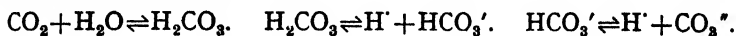
The constants governing these equilibria are, at $18°$:

$$\frac{[H_2CO_3]}{[CO_2]} = 7 \times 10^{-3}. \quad \frac{[H^{\cdot}][HCO_3']}{[H_2CO_3]} = 5 \times 10^{-5}. \quad \frac{[H^{\cdot}][CO_3'']}{[HCO_3']} = 6 \times 10^{-11}.$$

The calculation of the first constant is very difficult, since it involves no ions and is therefore inaccessible by the conductivity method, and when known it is useful only in combination with the second constant: $\dfrac{[H^{\cdot}][HCO_3']}{[CO_2] + [H_2CO_3]} = 3\cdot5 \times 10^{-7}$. The denominator is virtually the total concentration of carbon dioxide, free or combined, in the solution, and the figure $3\cdot5 \times 10^{-7}$ is the (apparent) first dissociation-constant of the acid, which is therefore very weak. If we take into consideration the fact that only $0\cdot7$ per cent of carbon dioxide dissolved in water is combined with it, the acid is seen to be a good deal stronger than it appears to be.

In its second dissociation carbonic acid is very weak, so that solutions of carbonates are strongly alkaline from hydrolysis. Bicarbonate solutions are also hydrolysed, and contain, in addition to bicarbonate ions, carbonate ions and free carbonic acid. Their hydrogen ion concentrations lie in the neighbourhood of 10^{-8} and 10^{-9}, according to the dilution, and they are consequently nearly neutral, so that carbonate solutions can be titrated with acid to bicarbonate with phenolphthalein, though not very exactly.

Carbonates, except those of the alkali-metals, ammonium and

*T

thallium, are insoluble in water. It is, however, usually impossible to precipitate them by passing carbon dioxide through neutral solutions of the salts of the metal, because the carbonate ion concentration of a solution of carbon dioxide in water is extremely small. A carbonate solution must be used instead. All bicarbonates, on the other hand, are soluble in water (though sodium bicarbonate is not very soluble). On this fact is based the usual test for carbon dioxide. When the gas is bubbled through lime-water, which has a distinctly alkaline reaction, on account of the basic properties of calcium hydroxide, finely-divided calcium carbonate is produced and the liquid becomes milky:

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow 2H^{\cdot} + CO_3'' \quad \text{and} \quad Ca^{\cdot\cdot} + CO_3'' \rightarrow CaCO_3 \downarrow,$$
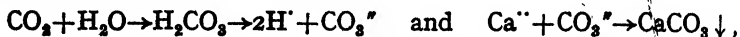
but on continuing the passage of the gas, bicarbonate is formed and the precipitate dissolves:

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{\cdot\cdot} + 2HCO_3'.$$

On heating, bicarbonates lose carbon dioxide and water and give the normal carbonate:

$$2HCO_3' = CO_3'' + H_2O + CO_2 \uparrow,$$
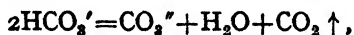
and this reaction takes place in water on boiling.

When, as is often the case, the carbonate and hydroxide of a metal are both insoluble, the addition of a carbonate solution to a solution of one of its salts usually precipitates a mixture of the carbonate and hydroxide, which may also include a basic carbonate of definite composition. The hydroxyl ions required for the precipitation of the hydroxide are derived from the hydrolysis of the carbonate solution, and it is often possible to precipitate the pure carbonate by the use of a bicarbonate solution, in which the hydroxyl ion concentration is very much less. In addition to this it is sometimes necessary to bubble carbon dioxide through the solution in which the precipitate is suspended. Metals such as aluminium, whose hydroxides are very weak bases, do not form carbonates.

On account of the acidic nature of carbon dioxide it combines with solid basic oxides or hydroxides at ordinary temperatures, e.g.:

$$CaO + CO_2 = CaCO_3 \quad \text{or} \quad KOH + CO_2 = KHCO_3,$$
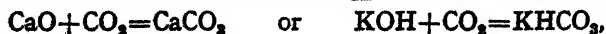
and carbon dioxide in a gas stream (as in organic analysis) is estimated by absorbing it in aqueous potash, which may be weighed before and after. To prevent increase in weight by absorption of water from the air, it is necessary to protect the potash bulb on the far side with a calcium chloride tube and to dry the gases before they enter it.

The constancy of the proportion of carbon dioxide in the atmosphere is due partly to the removal of the gas by the photosynthetic activity of green plants, and partly to the fact that the bicarbonates in the ocean act as carbon dioxide ' buffers,' and thus regulate the equilibrium between the dissolved gas and that present in the air.

Percarbonates.—These salts contain the ion C_2O_6''. Potassium percarbonate, $K_2C_2O_6$, is precipitated as blue crystals when a saturated solution of potassium carbonate is electrolysed at a low temperature. A diaphragm must be used, and the anode must be a smooth platinum wire, at which oxygen has a high over-voltage:

$$2CO_3'' - 2 \text{ electrons} = C_2O_6''.$$

On careful drying the salt is obtained as a white anhydrous solid soluble in water. Its solutions have strong oxidizing properties and behave as though they contained hydrogen peroxide, which indeed is probably formed by hydrolysis:

$$C_2O_6'' + 2OH' = 2CO_3'' + H_2O_2.$$
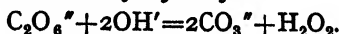
Percarbonates can also be obtained by the action of carbon dioxide on cold suspensions of sodium peroxide:

$$2CO_2 + Na_2O_2 = Na_2C_2O_6.$$

All percarbonates are unstable, and on warming give the normal carbonate, carbon dioxide, and oxygen:

$$2K_2C_2O_6 = 2K_2CO_3 + 2CO_2 \uparrow + O_2 \uparrow.$$

Halides.—*Carbon tetrafluoride*, CF_4, is prepared by union of the elements, or by the action of silver fluoride on carbon tetrachloride at 300°:

$$4AgF + CCl_4 = CF_4 + 4AgCl.$$

It is a colourless, odourless gas, boiling-point −130°. It is very stable and inert, being unaffected by water, concentrated sulphuric acid, caustic potash, or benzene, and suffers no change even when mixed with hydrogen and exposed to sparks. Sodium, magnesium, and barium react with it with incandescence.

The stability of covalent halides usually decreases from fluorine to iodine, and this is very noticeable in Group IV.

Carbon tetrachloride, CCl_4, cannot be obtained at any temperature by combination of the elements, and is prepared on a fairly large scale by the action of chlorine on carbon disulphide:

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$
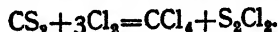
Iodine or anhydrous aluminium chloride may be used as catalyst. Carbon tetrachloride is a colourless volatile liquid, boiling at 77°, with a sweet smell, and is used in laundries in ' dry-cleaning,' and in

oil mills for extracting oil from crushed seeds; both these uses depend on its solvent power for oils and fats.   It is non-inflammable, and this is an advantage over carbon disulphide, which is sometimes used for the same purpose, but it is quite as poisonous, is dearer, and also attacks metal-work.   Both the disulphide and the tetrachloride are now being replaced as a solvent by 'westron,' or acetylene tetrachloride, $C_2H_2Cl_4$, and 'westrosol,' C_2HCl_3 (trichlorethylene). The latter has no deteriorating effect upon metals.

Carbon tetrachloride is a heavy liquid (density 1·5ð) and the vapour is five times as heavy as air.   Hence carbon tetrachloride is used in fire-extinguishers; it is immediately vaporized at the temperature of the conflagration.   It is particularly suitable for motor-car outfits, as it dissolves petrol, whereas water merely floats it.   It has also been used in shampooing, but is not to be recommended for this purpose, as its anaesthetic powers exceed those of chloroform.

In the laboratory it is used as an eminently inert solvent for oils, fats, the halogens, etc., and has the advantage of being practically insoluble in water.   The chemical stability of the substance is very remarkable; it is the only tetrachloride of Group IV to be entirely unaffected by water, and sodium has no visible action on it in the cold.   This inactivity is probably due to the symmetrical and fully saturated electronic structure (the covalency maximum of carbon is four) and should be contrasted with the ready hydrolysis of the tetrachloride of silicon, whose covalency maximum is six. The dielectric constant of carbon tetrachloride is small (2·0), it has negligible donor or acceptor properties, and is the non-polar solvent *par excellence*; it neither ionizes in other solvents nor induces ionization in substances dissolved in it.

Carbonyl chloride or Phosgene, $COCl_2$, is the acid chloride of carbonic acid.   It is produced by the combination of carbon monoxide and chlorine on a charcoal catalyst (in sunlight the action takes place spontaneously) or by oxidizing carbon tetrachloride with fuming sulphuric acid.   It is a colourless, extremely poisonous gas, boiling at 8° and slowly hydrolysed by water:

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

Carbon disulphide, CS_2, is prepared by heating coke and sulphur in an electric furnace, from which the carbon disulphide escapes as vapour.   It is an excellent solvent for oils and fats, sulphur, phosphorus, iodine, rubber, and other substances, and is used on the large scale in oil recovery and in the vulcanization of rubber.

It is a colourless volatile liquid, boiling at 46°, and highly inflammable.   The pure substance has a sweetish smell, but the commercial product contains impurities which give it a disgusting

odour: they can be removed by shaking with mercury and distilling. Carbon disulphide is only very slightly soluble in water.

Carbon oxysulphide, carbonyl sulphide, COS, is a colourless inflammable gas prepared by the combination of carbon monoxide and sulphur vapour in a hot tube, or more conveniently by the action of moderately concentrated sulphuric acid on a thiocyanate:

$$CNS' + 2H^{\cdot} + H_2O = NH_4^{\cdot} + COS \uparrow.$$
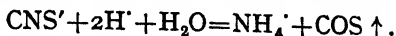
In physical properties it is intermediate between carbon disulphide and carbon dioxide.

Cyanogen, C_2N_2, is obtained by heating the cyanides of mercury, silver, or gold, e.g.:

$$Hg(CN)_2 = Hg + C_2N_2 \uparrow,$$
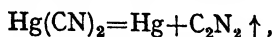
or by heating mixed solutions of cupric salts and cyanides:

$$Cu^{\cdot\cdot} + 2CN' = Cu(CN)_2 \downarrow \quad \text{and} \quad 2Cu(CN)_2 = Cu_2(CN)_2 + C_2N_2 \uparrow.$$
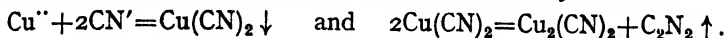
It is a colourless, inflammable, and extremely poisonous gas with a peculiar smell. It is fairly soluble in water, but the solution is unstable and the cyanogen is slowly hydrolysed with the formation of organic substances. With the alkali-metals cyanogen combines to form cyanides:

$$2K + C_2N_2 = 2KCN.$$
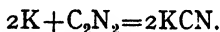
Paracyanogen is a polymer of cyanogen simultaneously produced when the gas is prepared by heating mercuric cyanide. It is a brown powder that yields cyanogen on strong heating.

Hydrogen cyanide, HCN, sometimes called *hydrocyanic* or *prussic acid*, is prepared by the distillation of a cyanide solution to which a dilute acid, such as dilute sulphuric acid, has been added. The product is an aqueous solution of hydrogen cyanide. If the substance is required pure the water-vapour must be removed by passage through calcium chloride; the hydrogen cyanide can then be condensed in a freezing-mixture. It can also be obtained by passing ammonia over carbon at a high temperature and rapidly cooling the gas stream after it leaves the reaction vessel:

$$NH_3 + C \rightleftharpoons HCN + H_2.$$
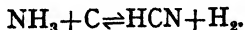
Hydrogen cyanide is a colourless liquid, boiling at 27°, with a peculiar odour to which many persons are completely insensitive. Like other cyanides it is intensely poisonous, and a few drops placed on the tongue usually cause practically instantaneous death. The resistance to the action of the poison varies with individuals, but cases have been recorded of suicides who have lost consciousness before putting down the cup from which the poison has been drunk. Nevertheless, South African natives, if allowed, use the

tanks of cyanide solution for the gold-mines as bathing pools and seldom suffer any ill effects.

Hydrogen cyanide mixes with water in all proportions. The solutions are very weakly acidic, the dissociation-constant of the acid being only 7×10^{-10}. Consequently solutions of cyanides, such as potassium cyanide, are strongly hydrolysed and have a marked alkaline reaction. By *concentrated* acids cyanides are decomposed with the formation of carbon monoxide and an ammonium salt:

$$CN' + 2H^{\cdot} + H_2O = NH_4^{\cdot} + CO \uparrow .$$
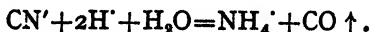
Cyanides are reducing agents, and in the exercise of this power are converted to cyanates:

$$CN' + O = OCN'.$$
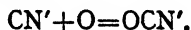
Their remarkable power of forming complexes of great stability has already been alluded to. It has been shown that the organic isocyanides have a structure in which six electrons are shared between the carbon and nitrogen atoms: the structure of the cyanide ion is:

$$: N \quad C :$$

In hydrogen cyanide the hydrogen atom may be attached either to the nitrogen or the carbon, and there is some reason to believe that the liquid is an equilibrium mixture of the tautomeric forms H.CN and H.NC. The complex-forming powers of the cyanide ion are specially enhanced because it contains two 'lone-pairs' (see p. 797), and in many solid cyanides both pairs are active.

SILICON

Si = 28·09. *Atomic Number*, 14

History.—VAN HELMONT (1577–1644) made silica (SiO₂) the basis of one of the earliest illustrations of the conservation of matter. He fused a known weight of silica with alkali, dissolved the ' glass' in water, and then precipitated the silica with acid. On drying and weighing, the weight of silica obtained was found to be equal to the original weight. BECHER (1655) regarded silica as an earth, if his *terra vitrescibilis* is rightly to be identified with that substance. TACHENIUS, however, in 1660 showed that it differed from an earth in possessing acidic properties. LAVOISIER (1787) assumed silica to be the oxide of an unknown element, and in 1809–11 GAY-LUSSAC and THENARD prepared crude silicon by heating potassium in silicon

fluoride gas (SiF$_4$). BERZELIUS (1823) obtained a better yield by reducing potassium fluosilicate (K$_2$SiF$_6$) with potassium, and was able to determine the atomic weight of the element. He regarded it as a metal, but DAVY showed it to be a non-metal and to possess a striking similarity to carbon.

Occurrence.—With the single exception of oxygen, silicon is the most abundant element on the face of the earth (including the atmosphere and the sea), and forms about one-quarter of the earth's crust, by weight, whereas oxygen accounts for about a half. It occurs exclusively as the dioxide, silica, SiO$_2$, or as a silicate. Flint, quartz (' rock-crystal '), and sand are all silica in different states of purity, and several precious stones, such as amethyst or jasper, consist of silica coloured by traces of other compounds. Silicates are very complex substances in which almost any metal may be contained; the aluminosilicates are particularly abundant and are the principal constituent of clay.

Silicon and its Compounds.—The chemistry of silicon is dominated by the stability of silica and the silicates, the final product of almost all the reactions in which it takes part. Silicon forms no elementary ions, and its compounds are nearly all either insoluble in water or are hydrolysed to form silica or a silicate. Silicon has the usual resemblance with the first member of the previous group, boron, and also strongly resembles carbon. Unlike carbon, the element does not occur in the free state in nature, and silicon is much more difficult than carbon to prepare, on account of the great stability of the dioxide. Silicon shows, though to a much smaller extent, some of the power which carbon has of forming long chains, but in the silicon chains oxygen atoms must alternate with the silicon atoms. Silicon is almost invariably quadrivalent, and in this it resembles carbon, though silicon monoxide is very far from playing a part of the same importance as carbon monoxide. The covalency maximum of silicon is six, compared with four for carbon, and this is probably responsible for the instability of the tetrahalides towards water and the existence of the fluosilicates; the great complexity of the silicates is due to the variety of ways in which SiO$_4$ tetrahedra can unite.

Elementary Silicon.—The element can be prepared by reducing either a tetrahalide or a fluosilicate with an alkali-metal:

$$4K + SiF_4 = 4KF + Si \quad \text{or} \quad 4K + K_2SiF_6 = 6KF + Si.$$
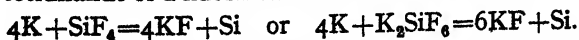
It can also be prepared, though in poor yield, by heating a mixture of sand and magnesium powder:

$$2Mg + SiO_2 = 2MgO + Si.$$

Magnesium silicide is produced at the same time. All these processes yield amorphous silicon. The crystalline element can be

obtained by heating a mixture of fluosilicate and magnesium in the proportions shown in the equation:

$$K_2SiF_6+2Mg=2KF+2MgF_2+Si,$$

or by reducing silica with calcium carbide. Crystalline silicon is also obtained as a by-product in the manufacture of carborundum.

Properties.—Silicon has a high melting- and boiling-point, but can be distilled with difficulty in the electric furnace. Crystalline silicon in appearance somewhat resembles a metal, and has some power of conducting the electric current, while with certain metals it forms alloy-like compounds, but it will not liberate hydrogen from any acid except hydrofluoric. Crystalline silicon has the crystal structure of the diamond, and shares some of the chemical inertness of carbon. If heated in air or oxygen it will burn to form silica, and will combine with fluorine at all temperatures to form the tetrafluoride, SiF_4, with the evolution of much heat, but it must be heated before combination with chlorine takes place. At high temperatures the reducing powers of silicon are more evident, and at a white heat it will decompose steam and many metallic oxides with the formation of silica. Silicon readily liberates hydrogen from caustic alkalis, either fused or in solution, with the formation of silicates. Just as diamond is less reactive than charcoal, so is crystalline silicon less reactive than the amorphous variety.

Silicides.—The silicides of two elements have attained some industrial importance, e.g. *carbon silicide*, or *carborundum*, which has already been described (p. 566), and *iron monosilicide, ferrosilicon*, FeSi, obtained by reducing silicate-containing iron ores in the electric furnace. Ferrosilicon is added to iron to improve its resistance to acids, and the resulting alloy finds an increasing use in the manufacture of resistant vessels for the concentration of sulphuric acid.

SILICON HYDRIDES.—These interesting compounds are prepared from magnesium silicide, just as the somewhat similar compounds of boron are prepared from magnesium boride. Magnesium silicide, Mg_2Si, is prepared by heating dry silica with a large excess of magnesium powder at a temperature which must not be allowed to rise too high, otherwise silicon is produced. The substance thus obtained is gradually added to dilute hydrochloric acid at 50° in an atmosphere of hydrogen (Fig. 120, p. 522), when a gas is obtained consisting chiefly of hydrogen, but also containing some 5 per cent of hydrides of silicon, of which the simplest is produced according to the equation:

$$Mg_2Si+4H^{\cdot}=SiH_4\uparrow+2Mg^{\cdot\cdot}.$$
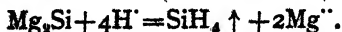
The mixed gases are freed from water and hydrogen chloride and

are then separated from hydrogen by condensing them with liquid air. The mixture is then fractionally distilled.

Silane, silicomethane, SiH_4, is a colourless gas with a peculiar smell, and is stable in the absence of air, but on strong heating decomposes into silicon and hydrogen. It is spontaneously inflammable, yielding water and silica. Silane is produced in theoretical yield by adding silicon tetrachloride to lithium aluminium hydride in ether solution (cf. diborane, p. 523). Silane is slowly decomposed by water:

$$SiH_4 + 2H_2O = SiO_2 \downarrow + 4H_2 \uparrow,$$
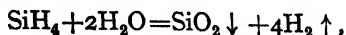
and more rapidly by solutions of caustic alkalis:

$$SiH_4 + H_2O + 2OH' = SiO_3'' + 4H_2 \uparrow.$$

By measuring the volume of hydrogen evolved in this and similar reactions, it is possible to analyse the silicon hydrides, of which a series is known, corresponding in formula with the lower paraffins, though the properties of the two series of compounds are not at all similar. Typical members are disilane, or silicoethane, Si_2H_6, and trisilane, or silicopropane, Si_3H_8.

By the action of the halogens on silane at low temperatures, such compounds as monoiodosilane, SiH_3I, and dibromosilane, SiH_2Br_2, can be obtained. They are decomposed by water, but the silico-alcohols resulting from their hydrolysis are unstable and lose water to form silicoethers or silicoaldehydes:

$$SiH_3I + H_2O = SiH_3(OH) + HI. \qquad 2SiH_3(OH) = (SiH_3)_2O + H_2O.$$

$$SiH_2Br_2 + 2H_2O = SiH_2(OH)_2 + 2HBr. \quad SiH_2(OH)_2 = SiH_2O + H_2O.$$
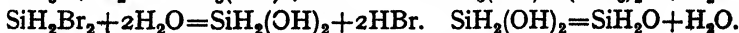
The hydrides of silicon are sharply distinguished from the paraffins by the action of hydrogen chloride, which has no effect on the latter, but reacts with the former, in the presence of aluminium chloride as catalyst, to form such compounds as monochlorosilane:

$$SiH_4 + HCl = SiH_3Cl + H_2.$$
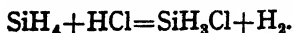
SILICON OXIDES.

Silica, silicon dioxide, SiO_2, constitutes some 12 per cent by weight of the crust of the earth, and if its derivatives the silicates are included, the proportion is more than half. It can be prepared in several amorphous and at least seven crystalline forms, of which we shall mention only the three most important: *quartz, tridymite,* and *cristobalite,* all of which are found in nature.

Quartz, or rock-crystal, is a very abundant mineral and is stable up to about 870°. Very large fine crystals of this substance are sometimes found. It is transparent not only to visible light but also to the radiations of the ultra-violet and infra-red which

are absorbed by glass, and is therefore ground into prisms and lenses and used in optical apparatus designed to deal with these wave-lengths. At 575° it is converted to a modification called β-quartz, to distinguish it from the α-quartz stable at ordinary temperatures. By X-ray analysis the two forms have been shown to differ in the arrangement of the atoms in the crystal lattice. At 870° it is converted to tridymite, a less dense substance whose temperature of formation is therefore increased by increased pressure, and at 1470° tridymite forms cristobalite, which melts at 1710°.

Fused silica, often called fused quartz or silica-glass, is prepared by fusing silica in the electric furnace. At a slightly higher temperature silica begins to vaporize. Amorphous silica is also obtained by the removal of water from silicic acid; it crystallizes on strong heating.

Silica is soluble in water only in the form of the colloidal solution silicic acid, which consists of silica associated with a variable quantity of water. The oxide has no amphoteric properties and is attacked only by hydrofluoric acid among the acids, and slightly by phosphoric acid at high temperatures. It will, however, dissolve in alkalis, amorphous silica in the solution, and quartz, slowly, in the fused substance:

$$SiO_2 + 2OH' = SiO_3'' + H_2O.$$
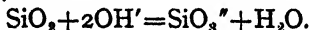
On account of its resistance to reagents fused silica is now a valuable material for vessels for use in the laboratory and in industry. It has been used on the large scale in the concentration of sulphuric acid. The coefficient of expansion of silica is exceedingly low, so that small articles made from it can be heated red-hot and quenched in water without cracking. It is also free from the traces of soluble impurity present in ordinary glass, and silica vessels are frequently used in research, especially when the catalytic properties of the surface are of importance, as in studies of reaction velocity. Laboratory silica-ware is made in two varieties, transparent and translucent; the former is more convenient but very much more expensive.

Silicic acid and silicates.—Hydrated silica is precipitated when an acid is added to the solution of a soluble silicate. The action may be written:

$$SiO_3'' + 2H' = H_2SiO_3 \downarrow,$$
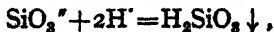
but the formula does not exactly represent the composition of the precipitate, which is in the colloidal form and is associated with a variable quantity of water. When purified by dialysis and protected from coagulation the solution is found to be a weak acid, easily precipitated by the addition of electrolytes.

Silicic acid and the silicates are for the most part complex substances of high molecular weight. The metasilicates of the alkali-metals are soluble in water; sodium metasilicate, Na_2SiO_3, is a colourless substance which can be obtained in the crystalline condition. The commercial product is manufactured under the name of 'waterglass' by boiling powdered flint under pressure with a concentrated solution of caustic soda and evaporating the solution to a syrupy consistency: the composition of the solute is approximately $Na_2Si_4O_9$, i.e. $Na_2O.4SiO_2$. It is used in the cardbox industry as an adhesive; for hardening cement roads; for mending small articles; and in dilute solution for preserving eggs— it clogs the pores of the shell and isolates the interior of the egg from bacterial infection. Silicate solutions contain the ions SiO_3'' and Si_2O_5''.

Glass is a mixture of various silicates, sodium, potassium, calcium, and lead being the metals most often used. Glass is undoubtedly to be regarded as an undercooled liquid, and has no definite crystalline structure, but it can sometimes be made to crystallize by prolonged heating. The process of crystallization is called 'devitrification,' and makes the glass brittle, translucent, and useless.

'Soft' or soda glass is made by heating sand, sodium carbonate, and lime in a glass-furnace. It softens at a lower temperature than other glasses and is the most widely used. If potash is substituted for soda the familiar 'hard' glass of the laboratory is obtained. Glasses specially made for resistance to attack by chemicals usually contain boric oxide and free silica—such are Jena glass and Pyrex. Finally, coloured glass is made by the addition of small quantities of metallic oxides or silicates, or even finely divided metals, to the melt, e.g. cobalt oxide, blue; chromium oxide, green; colloidal copper or gold, red. The 'stained glass' used in church windows consists of colourless glass on which a thin layer of coloured glass has been melted.

Silicon monoxide, SiO.—When a mixture of silica with silicon or carbon in the proportions SiO_2+Si or SiO_2+C respectively is heated in an electric furnace, the mixture is completely volatilized at 1400–1500°, that is, at a temperature far below that needed to volatilize either constituent alone. On slow cooling a brittle black solid, of composition SiO, is formed, but has been proved by X-ray diffraction to contain only silicon and its dioxide. It may be inferred that while a monoxide exists as vapour it decomposes on cooling and solidification. The brown amorphous powder produced by rapid cooling liberates hydrogen from water, and may retain some undecomposed monoxide:

$$SiO + H_2O = SiO_2 + H_2 \uparrow.$$
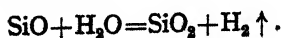
SILICON HALIDES.

Silicon tetrafluoride, SiF_4, can be made by the combination of the elements, or by the action of hydrogen fluoride on silica. The action:

$$SiO_2 + 4HF \rightleftharpoons SiF_4 + 2H_2O,$$

is reversible, and evolves heat when carried out from left to right; it is therefore necessary to prepare silicon fluoride at as low a temperature as possible. The equilibrium is complicated by the formation of fluosilicates (in which silicon has a covalency of six):

$$SiF_4 + 2F' \rightleftharpoons SiF_6''.$$
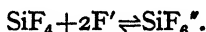
The fluoride is usually prepared by heating a mixture of silica and calcium fluoride with concentrated sulphuric acid, which by absorbing the water formed in the reaction promotes the formation of the tetrafluoride. The gas must be purified from hydrogen fluoride by passing it through a long tube full of red-hot glass wool, with which the hydrogen fluoride reacts to form water and silicon fluoride. It can be obtained pure by heating barium fluosilicate in a copper apparatus:

$$BaSiF_6 = SiF_4 \uparrow + BaF_2.$$

Silicon tetrafluoride is a colourless gas which, unlike carbon tetrafluoride, is immediately decomposed by excess of water into silica and hydrogen fluoride, though under suitable conditions the reverse action takes place. The silicon tetrafluoride then combines with the hydrogen fluoride formed by its hydrolysis to produce the soluble *fluosilicic acid*, so that the total reaction is:

$$3SiF_4 + 2H_2O = SiO_2 \downarrow + 2H_2SiF_6.$$
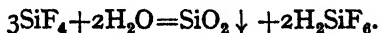
The delivery-tube from which the gas issues should dip under mercury under the surface of the water, or it will be choked by the gelatinous silica produced.

Fluosilicic acid, H_2SiF_6, has not been obtained pure, for on concentrating the solution hydrolysis takes place and the solution loses hydrogen fluoride and silicon tetrafluoride. It is a strong acid which can be titrated with caustic alkalis, and in solution in the cold shows very little tendency to decompose into fluorides of silicon and hydrogen. The fluosilicates cannot however exist in strongly alkaline solution, but are decomposed according to the equation:

$$SiF_6'' + 4OH' = 6F' + SiO_2 \downarrow + 2H_2O.$$
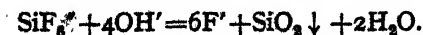
The fluosilicates of the alkali-metals (except lithium) and of barium are only slightly soluble.

Similar compounds are not known with halogens other than fluorine: most elements display their maximum covalency in combination with fluorine.

Silicon tetrachloride, SiCl$_4$.—Unlike carbon, silicon will burn in chlorine to form the tetrachloride, which can more easily be prepared by passing chlorine over a hot mixture of silica and charcoal. It is a colourless liquid (boiling-point 57°) which is slowly hydrolysed by water with the formation of silica and hydrogen chloride:

$$SiCl_4 + 2H_2O = SiO_2 \downarrow + 4HCl$$
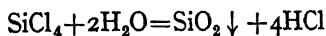
(contrast this behaviour with that of carbon tetrachloride). The liquid is unaffected by sodium, but when sodium is heated in the vapour silicon is obtained:

$$4Na + SiCl_4 = Si + 4NaCl.$$
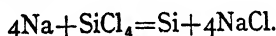
In addition to the tetrachloride, silicon forms compounds Si$_2$Cl$_6$, Si$_3$Cl$_8$, etc., with chlorine, which recall the higher chlorides of carbon.

Silicochloroform, trichlorosilane, SiCl$_3$H, is obtained by heating silicon, or better, copper silicide, in hydrogen chloride gas:

$$Si + 3HCl = SiHCl_3 + H_2.$$
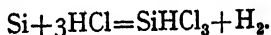
It is a volatile liquid which resembles silicon tetrachloride more than chloroform: it is quickly hydrolysed by water and is more reactive than chloroform.

Silicon tetrabromide, SiBr$_4$, and **silicon tetraiodide, SiI$_4$,** are colourless substances which resemble the tetrachloride, though the tetraiodide is a solid.

Silicon phosphate.—Silica dissolves with difficulty in hot phosphoric acid, forming a compound which has the composition SiP$_2$O$_7$. By excess of water it is hydrolysed into silica and phosphoric acid.

'Silicones.'—Highly polymerized organosilicon compounds, known collectively as 'silicones,' have become very important commercial products during the last few years. They are used for waterproofing, insulating, lubrication, and a wide variety of other purposes. Their constitution is that of indefinitely extended chains —e.g.:

$$-O-Si(CH_3)_2-O-Si(CH_3)_2-O-$$

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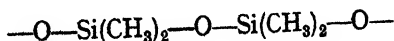
SUBGROUP

TITANIUM, ZIRCONIUM, CERIUM, HAFNIUM, THORIUM

</div>

[NOTE.—Cerium can be considered with the rare-earth group, but fits more conveniently into Group IV, as it has many features in common with thorium which distinguish it from the rare earths. With the exception of titanium, all the elements of this subgroup are rare.]

<div align="center">

TITANIUM

Ti=47·90.   *Atomic Number*, 22

</div>

Occurrence.—Titanium was discovered by GREGOR (1791), and independently by KLAPROTH (1794), but the metal itself in a state of reasonable purity has only recently been prepared. It is one of the most abundant of the metals, but though it is very widely diffused, ores rich in titanium are uncommon, and until the recent increased demand for titanium they have not been worked on a very large scale.

The principal ores are *rutile*, an impure form of titanium dioxide, found in North America and Norway, and *ilmenite*, iron titanate with excess of titanium dioxide, found chiefly in the United States, Brazil, and Southern India.

Uses.—In the form of *ferro-titanium*, an alloy containing some 80 per cent of iron, titanium has long been used for the ' cleansing' of steel, i.e. for the removal of oxygen and nitrogen. This demand is satisfied by quite small quantities of titanium, but the development of titanium pigments has greatly increased the output. Titanium paint is made either from the dioxide or from barium titanate, and has a greater covering power than white lead, is non-poisonous, unaffected by light, and unchanged by impurities in the atmosphere.

Compounds of titanium are also used as mordants in dyeing and in staining leather. The tervalent salts—the titanous compounds—are powerful reducing agents and are used in the dyeing industry as bleaches for removing the colour from goods that have been badly dyed—' stripping,' as it is called. In the laboratory they are used in volumetric analysis. Titanium tetrachloride is used in smoke-screens.

Extraction.—Ferro-titanium is made by two processes. If an alloy rich in carbon is required, ilmenite is reduced with carbon in the electric furnace. Ferro-titanium free from carbon is prepared by the Goldschmidt process.

Many processes have been devised for the preparation of titanium

compounds. In the MONK-IRWIN process ilmenite is ground up and heated in water-gas. The product is a mixture of iron and the dioxide of titanium, which is freed from iron by treatment with dilute sulphuric acid. The dioxide is then converted to the sulphate by fusion with sodium hydrogen sulphate, and the product is dissolved in water to form a solution from which fairly pure titanium dioxide can be precipitated by boiling. In the American process ilmenite is dissolved in hot sulphuric acid, and the ferric salts are then reduced to the ferrous condition. Titanium dioxide can then be precipitated from the solution by boiling it.

TITANIUM COMPOUNDS.—In its compounds titanium resembles silicon, but it is much more metallic and its compounds are more salt-like, while the titanates are less stable than the silicates. Silicon is never tervalent, but titanium has a well-marked series of tervalent salts, which give a violet ion Ti''' in solution, and which somewhat resemble the tervalent compounds of the neighbouring element vanadium.

The compounds in which titanium is quadrivalent are the most stable, but they can be reduced by strong reducing agents to the tervalent compounds, in which the metallic character of titanium is most clearly shown. By continuing the reduction compounds of bivalent titanium can be obtained, but these are very unstable and liberate hydrogen from water, while some of them burn in air.

Metallic titanium.—The hard, very brittle metal obtained by reducing the tetrachloride with sodium is finely powdered, and, mixed with iodine, is placed in an evacuated chamber heated to about 200° and traversed by tungsten filaments electrically heated to 1000°. On these the first-formed and volatilized tetraiodide is locally dissociated, and rods of metal develop round the filaments. As the rods thicken the heating current is increased to maintain the temperature. The process amounts to a distillation of titanium. So prepared the metal is freely malleable and ductile. When heated to a fairly high temperature in air, it burns to form the dioxide TiO_2, and at 800° it will also combine with nitrogen with incandescence to form titanium nitride, TiN. Titanium reacts with the halogens and the gaseous halogen acids to produce the tetrahalides, but in hydrochloric or sulphuric acid it liberates hydrogen and dissolves to form a violet solution which contains the tervalent ion Ti''' and is slowly oxidized by the air.

Oxides.—*Titanium monoxide*, TiO, is made by heating titanium dioxide with carbon in the electric furnace (compare the preparation of silicon monoxide). It is weakly basic.

Titanium sesquioxide, Ti_2O_3, is obtained by reducing the dioxide with hydrogen. When caustic alkali is added to the solution of a titanous salt such as $TiCl_3$, a reddish-brown precipitate of the

hydroxide $Ti(OH)_3$ is thrown down. It dissolves in sulphuric acid to give a violet solution of titanous sulphate, $Ti_2(SO_4)_3$.

Titanium dioxide, TiO_2, the most stable oxide of titanium, occurs in an impure form in nature as rutile. It may be precipitated from titanic solutions by alkalis, or from solutions of titanates simply by boiling them (hydrolysis). At low temperatures the precipitate may consist of the tetrahydroxide $Ti(OH)_4$, sometimes called orthotitanic acid, but X-ray diffraction fails to reveal any definite hydroxides of titanium. It can be converted to the dioxide by strong heating.

Titanium dioxide is produced when titanium burns in air or oxygen, and can be reduced to the metal only with the greatest difficulty, in which it resembles silica. It is amphoteric and when in the hydrated form will dissolve in acids to produce titanic compounds, probably giving rise to the colourless titanyl ion TiO'', and in alkalis to produce the titanates, whose characteristic ion is TiO_3'' or some more complex form. Titanic acid is so weak that the solubility of titanium dioxide in aqueous alkalis is very limited, and the titanates are best prepared from the dioxide and fused alkalis or carbonates. Like silicic acid, titanic acid can in solution exist only as a colloid, and is precipitated from solutions of titanates on boiling.

The *titanates* are often found associated with the silicates: calcium titanate occurs in the Ural Mountains, and ferrous titanate, $FeTiO_3$, is the principal constituent of the mineral ilmenite. As a typical soluble titanate we may mention potassium metatitanate, $K_2TiO_3.4H_2O$, prepared from titanic acid and fused caustic potash:

$$Ti(OH)_4 + 2KOH = K_2TiO_3 + 3H_2O.$$
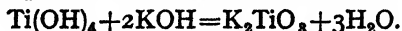
It is a colourless hygroscopic solid, whose solutions have a strongly alkaline reaction from hydrolysis.

Titanium trioxide or peroxide, TiO_3, in the hydrated form also called *pertitanic acid*, is obtained as a yellow precipitate by adding hydrogen peroxide to a solution of titanium disulphate, $Ti(SO_4)_2$, in sulphuric acid and then neutralizing with ammonia. Before the ammonia is added the solution is orange and possibly contains a per-acid. Since solutions of titanium disulphate are obtained by dissolving the dioxide in sulphuric acid, the net change may be represented:

$$TiO_2 + H_2O_2 = TiO_3 + H_2O.$$

The orange-coloured solution is used as a test both for titanium and for hydrogen peroxide. The colour is destroyed by reducing agents, and the trioxide is a fairly powerful oxidizing agent which will liberate chlorine from hydrochloric acid.

Titanium nitrides.—At a high temperature titanium will burn

in nitrogen to produce a nitride, and if titanium dioxide is reduced in ammonia gas the oxygen can actually be replaced by nitrogen, a very unusual reaction:

$$6TiO_2 + 8NH_3 = 6TiN + 12H_2O + N_2.$$
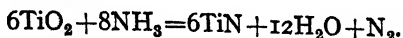
At lower temperatures the nitride of titanium is hydrolysed by water with the formation of titanium oxides and ammonia. It is golden-brown in colour, and as hard as diamond.

Halides.—*The tetrahalides.*—These are the most stable halides of titanium. The tetrafluoride $TiF_4.2H_2O$ is a colourless hygroscopic solid of definitely salt-like character which readily forms complexes, called fluotitanates, with other fluorides:

$$TiF_4 + 2F' = TiF_6''.$$
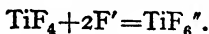
The fluotitanates are stable compounds which recall the fluosilicates, and, like potassium fluosilicate, potassium fluotitanate is only slightly soluble in water.

The tetrachloride $TiCl_4$ is one of the most important compounds of titanium, and is obtained by the action of chlorine on the metal or on a mixture of its oxides with carbon (compare aluminium), or, better, by heating the dioxide in the vapour of carbon tetrachloride:

$$TiO_2 + CCl_4 = TiCl_4 + CO_2.$$
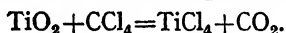
It is a liquid boiling at 135°, and as it can be thoroughly purified has been used in the determination of the atomic weight of titanium. In its behaviour with water it is intermediate between the tetrachlorides of silicon and tin; the reaction gives out much heat, but hydrolysis is not complete and an equilibrium is set up between titanyl ions TiO'' and the products of hydrolysis, of which the final stage is the formation of TiO_4'''', the orthotitanate ion. On boiling the solution hydrolysis is complete, unless there is a large excess of hydrochloric acid.

The tetraiodide TiI_4 readily burns in air, forming titanium dioxide and iodine:

$$TiI_4 + O_2 = TiO_2 + 2I_2 \uparrow.$$
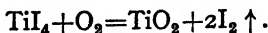
The *trihalides* are not much less stable than the tetrahalides and are the most definitely salt-like compounds of titanium. When a hydrochloric acid solution of titanium tetrachloride is reduced with aluminium or electrolytically, a violet solution is produced which contains *titanium trichloride*, $TiCl_3$. The anhydrous salt forms violet crystals, which are hygroscopic and which, like their solutions, are readily oxidized and decolorized by the air. Titanous chloride solutions are powerful reducing agents. The oxidation potential of Ti'''/TiO'' is (in N-acid) $+0.10$ volt. They will precipitate copper, silver, gold, or mercury from solutions of their

salts, reduce nitrates to ammonia, perchlorates and chlorates to chlorides, chromates to chromium salts, etc., and are now used to an increasing extent in the titration of ferric salts, which they reduce to ferrous salts, with ammonium thiocyanate as internal indicator:

$$Ti^{\cdots}+Fe^{\cdots}+H_2O=\ TiO^{\cdot\cdot}+Fe^{\cdot\cdot}+2H^{\cdot}.$$

They are also used in the titration of organic nitro-compounds, which they reduce to amines. As the solutions are oxidized by the air they must be stored under hydrogen, as shown in the diagram. Nowadays titanous chloride is usually replaced by titanous sulphate, obtained by the electrolytic reduction of a solution of titanium dioxide in sulphuric acid. In either solution excess of acid must be present to prevent hydrolysis.

FIG. 127. STORAGE OF TITANOUS CHLORIDE SOLUTIONS

Titanous bromide, TiBr$_3$, is produced together with the dibromide TiBr$_2$ when titanium is carefully heated in hydrogen bromide gas. These compounds are decomposed at higher temperatures, the final product being the tetrabromide:

$$2TiBr_3=TiBr_2+TiBr_4. \qquad TiBr_2=Ti+TiBr_4.$$
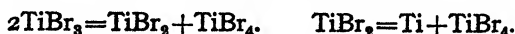
The *dihalides* are very unstable compounds obtained by reducing the trihalides with hydrogen:

$$2TiCl_3+H_2=2TiCl_2+2HCl.$$
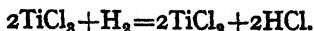
Titanium dichloride hisses violently when brought into contact with water, and liberates hydrogen from it:

$$TiCl_2+4H_2O=Ti(OH)_4+2HCl+H_2\uparrow.$$
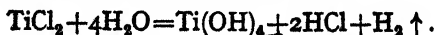
It also burns in air, forming the dioxide and the tetrachloride:

$$2TiCl_2+O_2=TiO_2+TiCl_4.$$
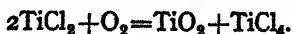
Sulphates.—The disulphate Ti(SO$_4$)$_2$ is obtained in solution by boiling the hydrated dioxide with sulphuric acid. When electrolytically reduced it yields the violet solution of titanous sulphate, Ti$_2$(SO$_4$)$_3$, in sulphuric acid used in volumetric analysis.

ZIRCONIUM AND HAFNIUM

$Zr = 91 \cdot 22$; *atomic number*, 40. $Hf = 178 \cdot 5$; *atomic number*, 72

ZIRCONIUM AND HAFNIUM.—These elements are separated in the Group IV list (p. 556) by cerium, but they resemble each other so closely that they will be treated together, while cerium and thorium, which also resemble each other, will be discussed in the next section.

Zirconium was discovered by Klaproth in 1789 in an investigation of the mineral *zircon*, from Ceylon, and was considered a very rare element until 1892, when a new mineral, *baddeleyite*, from Brazil, was found to contain some 90 per cent of the dioxide. In spite of this discovery zirconium may still be regarded as one of the scarce elements, as it is very little used in commerce and only small quantities of the ore are extracted.

Impure zirconia (zirconium dioxide) is also found in Norway, and is contained in the precious stone called *jargon* found in Ceylon. The zirconia of commerce is, however, nearly all obtained from baddeleyite, which is finely ground and extracted with boiling hydrochloric or sulphuric acids, which remove most of the iron and titanium with which the zirconia is associated.

The credit for the discovery of *hafnium* was the subject of a controversy into which we need not enter. URBAIN claimed that the new element was the same as an element which he identified in 1911 and named *celtium*, whereas the credit is generally assigned to COSTER and HEVESY, who published their work in 1923 and were certainly the first to prepare and investigate hafnium compounds. The name is derived from Hafnia, the Roman name for Copenhagen. The conclusive evidence for the existence of the new element was its X-ray spectrum, which proved that its atomic number must be 72 and that its place must therefore be among the elements of Group IV. The metal has since been shown to be rather less rare than was at first supposed, and accompanies zirconium in most of its ores, sometimes to the extent of nearly 30 per cent.

The close resemblance between element No. 72 and zirconium was predicted by BOHR, on the basis of his theory of atomic structure (Chapter X), before the discovery of hafnium. He thus emulated the feat of Mendeleeff.

Zirconium compounds have not as yet attained much commercial importance. The dioxide ZrO_2 resembles silica in having a very low coefficient of expansion, and is even more refractory; it is therefore used to a limited extent in the manufacture of crucibles for high-temperature work and for furnace linings. Zirconium has a fairly high atomic weight and hence a high absorbing power for

X-rays, and as its compounds are non-poisonous they are used for defining the intestines of patients requiring abdominal X-ray examination. The patient swallows a preparation of pure zirconium dioxide, which casts a heavy shadow in the X-ray photograph. (Bismuth nitrate is more commonly used for the same purpose.) Hafnium has as yet no commercial use.

ZIRCONIUM AND HAFNIUM COMPOUNDS.—The very close resemblance between these elements can be paralleled only in the neighbouring rare-earth group, and was responsible for the long delay in the recognition of hafnium as a separate element. Their compounds can be separated only by the technique developed in the study of the rare earths, and fractional precipitation or crystallization is generally employed. The chemistry of hafnium compounds has not yet been exhaustively investigated.

Both elements resemble titanium and silicon, and in the predominance of quadrivalency they are intermediate between the two, for while tervalent compounds of zirconium are known, they have not the stability of the corresponding compounds of titanium. Zirconium is more metallic than either silicon or titanium, its oxide is more basic, its salts are less hydrolysed in solution, and it is distinguished by a greater tendency to produce zirconyl compounds, containing the bivalent radical ZrO, which perhaps also exists in solution as a bivalent ion.

Metallic zirconium and hafnium.—In the preparation of these metals the same difficulties are encountered as with titanium and the same method has been successful: the reduction of the tetrachloride with sodium, followed by ' distillation ' on to tungsten filaments (see p. 589). For these metals the chamber temperature is 600° and that of the filaments as high as 1800°.

Zirconium is a hard white metal which will take a high polish: it can be worked as easily as copper. It dissolves with difficulty in acids, of which hydrofluoric acid or phosphoric acid are the most suitable. It will combine, though not very readily, with oxygen or nitrogen to form the dioxide or nitride, or with the halogens to form the tetrahalide.

Oxides and hydroxides.—Only the dioxide and its hydrated forms are important. It can be obtained either by purification of zirconium ores, or by burning the metal in oxygen, or by precipitating zirconium salts with caustic alkali either as orthozirconic acid, $Zr(OH)_4$, or as metazirconic acid, $ZrO(OH)_2$. It is amphoteric, and will dissolve in acids to give the quadrivalent zirconium salts, or in fused caustic alkalis to give the zirconates:

$$ZrO_2 + 2OH' = ZrO_3'' + H_2O.$$
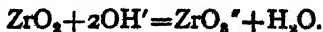
Its solubility in aqueous solutions of the caustic alkalis is only

slight, and the zirconates, as salts of a very weak acid, are strongly hydrolysed in solution and have an alkaline reaction. In all these respects zirconium dioxide resembles titanium dioxide: it cannot, however, be reduced with hydrogen.

Halides.—The tetrahalides are more salt-like than the corresponding compounds of titanium, and the lower halides are far less stable and need not be considered here.

The *tetrachloride* $ZrCl_4$ is prepared by the two methods given for preparing titanium tetrachloride, but it differs from this compound in being a crystalline solid which sublimes at 300°. When added to water it gives out much heat, but hydrolysis is not complete, the product being the soluble compound zirconyl chloride:

$$ZrCl_4 + H_2O = ZrOCl_2 + 2HCl.$$
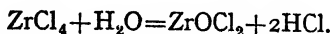
Zirconium nitrate.—The normal nitrate cannot be obtained by dissolving the dioxide in nitric acid, as the soluble compound zirconyl nitrate, $ZrO(NO_3)_2$, is produced. The solutions are much hydrolysed and slowly deposit a basic nitrate.

Zirconium sulphate.—Hydrated zirconium dioxide will dissolve in concentrated sulphuric acid, and from the solution crystals of the sulphate $Zr(SO_4)_2.4H_2O$ can be obtained by evaporation. This substance dissolves freely in water to form a solution with peculiar properties; it does not respond to the tests for the quadrivalent zirconium ion $Zr^{....}$, and the molecular weight of the solute, as determined by the freezing-point method, shows it to be dissociated into four ions. Moreover on electrolysis the zirconium is carried to the anode, which proves that it must be present in the anion, but the nature of this anion is still uncertain.

CERIUM AND THORIUM

Ce=140·13; *atomic number*, 58. Th=232·05; *atomic number*, 90

CERIUM AND THORIUM.—In some systems of classifying the elements cerium and even thorium are included among the rare earths; but thorium is a normal member of the fourth group and cerium resembles it so closely that the elements are best considered together in this group.

Cerium was discovered in 1803 in a mixture of rare earths, but thorium was not identified until 1824 (BERZELIUS). For sixty years they were among the rarest and least important of the known elements, but in 1885 AUER VON WELSBACH invented the incandescent gas-mantle, and thorium and cerium immediately became of commercial importance. A hurried search was at once instituted

for sources of supply beyond the scanty deposits of thorium-containing minerals in Norway, and a rich deposit of *monazite sand*, containing about 5 per cent of thorium as phosphate and the less important cerium phosphate, was discovered on the coast of Brazil, and remains to this day the largest source of thorium compounds in the world. For a time thorium rivalled coal and oil as the object of international intrigue, and the control of the industry passed largely into German hands, but since that date deposits have been found at Travancore (in the south of India) and elsewhere.

In all these deposits thorium is associated with cerium and the rare earths: the thorium is extracted and the residues are the only important source of the rare earths, for which in recent years it has been possible to find some small commercial use. The lighter and worthless parts of the mineral are first washed away by air or water while the mineral is shaken on vibrating tables, and some kind of magnetic separation is then effected, as the thorium and rare-earth minerals are attracted to a slight extent by a magnet. The separated material is then shipped to the place of treatment, where the thorium is extracted. Since the properties of thorium much resemble those of the rare earths, this is a difficult matter. The phosphates are first dissolved in hot concentrated sulphuric acid, the solution is diluted, and insoluble impurities are removed. The solution is then cautiously neutralized. Thorium is the most basic of all the metals present, hence practically the whole of it is contained in the first fractions of the phosphate precipitate. These fractions are then fused with sodium carbonate and extracted with water, which dissolves sodium phosphate and leaves the insoluble thorium dioxide behind. This residue is again dissolved in sulphuric acid and the thorium separated by one (or more) of three processes:

(i) Fractional crystallization of the sulphates.

(ii) Addition of excess of an alkaline carbonate: thorium remains in solution as a complex carbonate while the rare earths are precipitated.

(iii) A similar process involving a complex thorium oxalate.

The thorium is then precipitated as the dioxide and converted to the nitrate, $Th(NO_3)_4.4H_2O$, which is sold to the mantle manufacturers. The residues from these processes, when it is no longer profitable to extract thorium from them, are worked up for cerium and sometimes for other rare earths. Mesothorium (p. 310) is also obtained as a by-product. Mixed with zinc sulphide it is used on the dials of luminous clocks and watches.

The Incandescent Gas-mantle.—Before 1885 coal-gas was burned without an air-supply at the jet, and the luminosity of the flame,

weak as it was, was chiefly due to the unsaturated hydrocarbons (mostly ethylene) present in the gas. Von Welsbach found that a cotton mantle heated by a gas-jet gave out a feeble light which was greatly intensified if thorium dioxide had been deposited on it. In an effort to secure the best results he purified the thorium compound used for this purpose, but discovered that purification reduced the intensity of the light. The effect was traced to cerium, and von Welsbach's best mixture, which contained 99 per cent thorium dioxide and 1 per cent cerium dioxide, has never been improved on, and is still in use on the diminishing number of gas-mantles that are consumed every year.

The fabric of the early mantles was made from cotton or ramie fibre, but artificial silk is now largely employed. The mantle is soaked in a concentrated solution of thorium nitrate (with 1 per cent cerium nitrate and various strengtheners), wrung out, dried, and heated in a gas flame, which converts the nitrates to oxides and also causes the mantle to shrink. It is further strengthened by soaking in collodion, and is tested in a machine which administers up to six hundred shocks a minute to the support.

Uses of cerium.—Von Welsbach also discovered that certain alloys of cerium with the rare earths, when struck with hard steel, gave off sparks which could be used to light gas or petrol. He sold his invention for £30,000, and the various alloys, such as 'Auer' metal, or 'Mischmetal,' are used in automatic gas-lighters and in cigarette-lighters. The pyrophoric properties are improved by the addition of some 35 per cent of iron to the alloy, which is made by electrolysis of the fused chlorides of the rare-earth metals, and in which some two hundred tons of rare-earth oxides are consumed per annum. Pyrophoric alloys are also attached to shells to define their flight; the friction of the air raises them to incandescence soon after leaving the gun. The only other industrial use of cerium of any importance is the preparation of electrodes for arc lights: the luminosity of carbon electrodes is improved by soaking them in a solution of cerium fluoride.

CERIUM AND THORIUM COMPOUNDS.—The chemistry of thorium is simpler than that of any other element in the fourth group, partly because in nearly all its compounds it is quadrivalent, and partly because it is the most metallic member. The oxide is not amphoteric and shows slight tendency to complex formation, but the thoryl ion ThO¨, recalling the zirconyl ion ZrO¨, occurs very frequently. The quadrivalent compounds of cerium resemble those of thorium, but are very much less stable, and cerium is most stable in the tervalent condition, as are all other members of the rare-earth family. The change $Ce^{····}+electron \rightleftharpoons Ce^{···}$ is easily reversible and is used in volumetric analysis (see ceric

sulphate); in this reaction cerium resembles titanium and is the only rare-earth element to display a well-marked valency of four. As is usual with the rare earths, the trihydroxide is a strong base, and the (tervalent) cerous salts are only slightly hydrolysed, whereas the tetrahydroxide is a weaker base than thorium hydroxide, and the ceric salts are considerably hydrolysed and have to be kept in solution by acids. The ceric ion is yellow, the cerous ion colourless. To its rare-earth character cerium owes the power of forming a normal carbonate (in which it is tervalent): this distinguishes it from all other members of the subgroup. Metallic cerium is also the softest and most reactive metal of the subgroup and has by far the lowest melting-point.

Metallic cerium and thorium.—Cerium is made by the electrolysis of a fused mixture of cerous chloride and fluoride. It is a soft grey metal, melting at 635°, which burns in air at 160° with a light more intense even than that of magnesium, producing a mixture of the oxide and nitride. It liberates hydrogen from dilute acids and even from boiling water, and it combines with the halogens to form cerous halides.

The electrolytic method has not been successfully applied to thorium, which is made by reducing the tetrachloride with sodium. It is an iron-grey powder, melting at about 1730°, which burns in air at a red heat. It will dissolve in acids but is unaffected by water: heated in nitrogen it produces the nitride, Th_3N_4, and with the halogens thorium tetrahalides are formed.

Oxides and hydroxides.—*Cerous hydroxide*, $Ce(OH)_3$, and *ceric hydroxide*, $Ce(OH)_4$, are precipitated when caustic alkalis are added to solutions of cerous and ceric salts: the former is white, the latter yellow. Cerous hydroxide is readily oxidized by the air to the ceric compound. Both hydroxides are basic and dissolve in acids, but not in alkalis, to give colourless or yellow solutions respectively.

Thorium hydroxide, $Th(OH)_4$, is obtained in a similar way. No lower oxide or hydroxide is known. It is soluble in acids but not in alkalis. The anhydrous oxide ThO_2 has been used on the commercial scale as a catalyst for gas reactions.

Both cerium and thorium precipitate *peroxides*, $CeO_3.nH_2O$ and $ThO_3.nH_2O$, when solutions of their salts are treated with hydrogen peroxide.

Halides.—Since the oxidation potential of the reaction $Ce^{\cdots} \rightarrow Ce^{\cdots}$ is sufficient to discharge all the halide ions except fluorides, the only tetrahalide of cerium is the fluoride CeF_4.

Cerous chloride, $CeCl_3$, is made by heating the oxide in the vapour of carbon tetrachloride, and is a colourless solid melting at 850°, and soluble in water to give a nearly neutral solution. Ceric oxide will dissolve in hydrochloric acid only if a reducing agent is present,

and ceric chloride is unknown, but *ceryl chloride*, $CeOCl_2.10H_2O$, has been prepared.

Thorium tetrachloride, $ThCl_4$, is prepared from the oxide by the methods used for the chlorides of titanium, zirconium, and cerium. *Thoryl chloride*, $ThOCl_2$, is an intermediate product of the reaction. The tetrachloride is a very hygroscopic solid of high melting-point and unmistakably salt-like character: it is insoluble in most organic solvents and is ionized in water.

Sulphates.—*Cerous sulphate*, $Ce_2(SO_4)_3$, is obtained by dissolving the trihydroxide in sulphuric acid. When ceric oxide is boiled with concentrated sulphuric acid a deep yellow powder is obtained—*ceric sulphate*, $Ce(SO_4)_2$—readily soluble in water. The solution, which should contain free sulphuric acid to prevent hydrolysis, is deep yellow in colour and is finding an increasing use in volumetric analysis: in colourless solutions no indicator is required. The solution has an oxidizing potential ($+1.6$ volts) about equal to that of potassium permanganate, and it has the advantages that it is stable and that it can be used in dilute (though not in concentrated) hydrochloric acid. Its principal use is in the oxidation of ferrous to ferric ions, which gives exact results:

$$Ce^{....}+Fe^{..}=Ce^{...}+Fe^{...}.$$
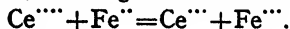
Thorium sulphate, $Th(SO_4)_2$, is prepared from the dioxide and sulphuric acid and is very soluble in water. The solution has a slight acid reaction from hydrolysis, and if titrated against a strong base with phenolphthalein gives an end-point corresponding with the formation of thoryl sulphate, $ThOSO_4$:

$$Th^{....}+2OH'=ThO^{..}+H_2O.$$
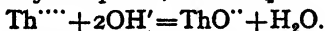
Nitrates.—*Ceric nitrate* is unknown; the *cerous* compound, $Ce(NO_3)_3.6H_2O$, is obtained from the trihydroxide and nitric acid. *Thorium nitrate*, $Th(NO_3)_4.12H_2O$, is made from the dioxide and nitric acid; thorium comes into commerce in this form.

The radioactive properties of thorium have been described in Chapter X.

<div align="center">

Subgroup B

Germanium, Tin, and Lead

Germanium

$Ge=72.6$.   *Atomic Number*, 32

</div>

Occurrence.—In 1886 Winkler analysed a recently discovered mineral, *argyrodite*, from Saxony, and was unable to make his analysis total correctly: he found 93 per cent instead of 100 per cent. The discrepancy was proved to be due to the presence of

U

a new element which he called *germanium*: argyrodite is a double sulphide of germanium and silver, $4Ag_2S.GeS_2$.

In many respects germanium is intermediate between silicon and tin, and its properties were found to be in excellent agreement with the predictions of MENDELEEFF (p. 302). It also has some resemblance with arsenic, though its compounds are not toxic. It is the first definitely metallic member of the series C—Si—Ge—Sn—Pb, and has a stable valency of four and a less stable valency of two. The bivalent germanous salts are reducing agents which will bleach litmus and reduce chromates or permanganates.

Traces of germanium have been found in many substances (including the mineral water at Vichy), but few abundant sources are known, and the supplies of argyrodite are exhausted: it is therefore one of the rarest of the elements. Residues from zinc smelting are the chief present source. The recent discovery of the uses of germanium in electronic rectifiers and in the so-called transistors has much stimulated search for sources and methods of extraction.

Elementary germanium.—Germanium is made by heating the dioxide in hydrogen at 900°. So formed it is a light, very brittle element, melting at 958°, and with the diamond crystal structure. It does not readily dissolve in acids (except nitric acid), but will liberate hydrogen from fused caustic potash.

Hydrides.—*Germanium tetrahydride*, GeH_4, is a gas produced in poor yield when germanium solutions are reduced with nascent hydrogen. It is decomposed into its elements by heat, and resembles silicon tetrahydride, but is less stable. Compounds Ge_2H_6 and Ge_3H_8, recalling the higher hydrides of silicon, are also known.

Oxides and hydroxides.—Germanous hydroxide, $Ge(OH)_2$, is produced as a yellow solid by the action of water upon germanous chloride. It is said to be amphoteric, and will certainly dissolve in acids to give germanous salts, but no convincing evidence has been advanced for the existence of germanites. On heating (in nitrogen) the hydroxide yields the black monoxide, GeO, which is readily volatile at 700°, and for this reason is troublesome in reducing the dioxide to the metal.

Germanic oxide, GeO_2, is obtained by heating the lower oxide in air, or by the hydrolysis of germanic compounds. It is a white powder nearly insoluble in water and is amphoteric, but the acidic character predominates. The position of germanium between tin and silicon is emphasized by the fact that its dioxide is dimorphous, one form being similar to cassiterite, SnO_2, and the other to quartz.

Halides.—The tetrahalides are volatile covalent compounds, soluble in organic liquids but hydrolysed by water. The hydrolysis is, however, incomplete, and the halides are less hydrolysed than those of silicon.

Germanium tetrafluoride, GeF$_4$, is a colourless fuming gas prepared by heating barium fluogermanate, BaGeF$_6$, to 700°. It boils at —15°. Barium fluogermanate is precipitated by adding a barium salt to a solution made from germanium dioxide and hydrofluoric acid.

Germanous chloride, GeCl$_2$, resembles stannous chloride, but is a stronger reducing agent.

Germanochloroform, GeHCl$_3$, is prepared by passing hydrogen chloride over warm germanium. It is a liquid which is hydrolysed by water to form germanous hydroxide.

Sulphides.—*Germanous* and *germanic sulphides* can be precipitated by hydrogen sulphide from germanous and germanic solutions.

TIN

Sn=118·7. *Atomic Number,* 50

History.—If, as has been suggested, the Latin *stannum* is derived from *stan*, the Phoenician name for tin, the word was wrongly applied by the Romans, for their ' stannum ' appears to have been an alloy. The Latin name for tin was *plumbum candidum*, i.e. ' white lead,' and in Roman times the metal is supposed to have been shipped from the Scilly Islands and Cornwall by Phoenician traders. The apparent similarity between tin and lead was the cause of much confusion in ancient times, and it is frequently difficult to decide which of the two metals is indicated when the single word *plumbum* is used.

The use of bronze, which is an alloy of copper and tin, dates from prehistoric times, and was well established in ancient Egypt, Mesopotamia, India, and China. Its discovery was no doubt accidental, due to the smelting of a natural mixture of copper and tin ores; but early man soon discovered its composition, and tin ore deposits were then systematically exploited. The earliest definite records of tin-working in England are of the year 1198. The tin was smelted twice, once near the tin field, and again—for refinement—at special places and in the presence of the officers of the Stannaries, e.g. at Bodmin, Lostwithiel, Truro, and Tavistock.

The allotropic modification of tin, known as *grey tin*, was first noticed by ARISTOTLE (384–322 B.C.).

Occurrence.—Tin is less abundant than its extensive use might lead one to suppose; less abundant, for instance, than titanium. The only important ore is the dioxide SnO$_2$, which occurs in an impure form as *cassiterite, tinstone*, or *black tin*, in the Malay Peninsula, Bolivia, Mexico, and elsewhere. The Malay Peninsula accounts for about a third of the world production. The tin mines of Cornwall have been worked for centuries, but are now unimportant.

Extraction.—The ore is crushed, and sand or earthy matter removed as far as possible by washing. The concentrated ore is then roasted, to convert arsenides and sulphides to oxides; the arsenic may be condensed from the vapours as arsenious oxide. After the roasting the ore is sometimes freed from iron and tungsten in a magnetic separator; this avoids losses by alloying at a later stage. The ore is then well mixed with anthracite and heated in a reverberatory furnace. The molten tin collects at the bottom and is run off and cast into blocks (' block tin ') which are about 99·5 per cent pure. The slags are usually worked up for tin in blast-furnaces. The metal can be refined by heating it on a sloping bed, from which the molten metal runs; it is then stirred with green wood and skimmed.

Large quantities of tin are recovered from tinplate by electrolysis. The scrap tinplate is held in a wire basket and made the anode in a boiling solution of sodium sulphide, which is strongly alkaline by hydrolysis. The tin dissolves and is recovered from the solution in a state of purity by electro-deposition on a tin cathode. In an alternative method the scrap is exposed to chlorine gas, which converts the tin to the volatile stannic chloride.

Tin is used almost exclusively as the metal or in alloys. On account of its resistance to corrosion it is used in the manufacture of tinplate articles, which are made of steel dipped in molten tin and then pressed between rollers. Tin is malleable enough to be pressed into foil, which is used for wrapping cigarettes, confectionery, etc. (' silver paper ').[1] It is the best metal (excluding the platinum group or the precious metals) for use in stills for conductivity-water; it is quite unaffected by a mixture of air and water, even when the latter contains ammonia in solution.

The *alloys* of tin are of great commercial importance. *Pewter* contains about 75 per cent tin and 25 per cent lead. *Bronze*, *bell-metal*, and *gun-metal* are alloys of tin and copper in different proportions. *Tin amalgam* is used in mirrors. Among the low-melting alloys *solder* is perhaps the most important; it may contain tin and lead in almost any proportions—pure tin, indeed, can be used for soldering. Most alloys with low melting-points, such as those used in linotype machines, contain tin and lead as ingredients.

Properties.—Tin is a lustrous white metal which is not corroded by air or water. In hardness it is intermediate between lead and zinc. It is ductile, and can be pressed into foil or drawn into wire. The crystalline structure can be demonstrated by etching a tin surface with a mixture of concentrated hydrochloric acid and chlorine. If a bar of tin is bent, a faint sound called ' tin cry ' is

[1] Much 'silver paper' is now made of aluminium foil.

heard; it is believed to be due to the rubbing of the tin crystals together (but see *Nature*, 1932, *passim*).

It has been mentioned on p. 261 that tin exists in two allotropic modifications with a transition-point at 13°. A further allotrope called γ-tin exists above 161°. Tin melts at 232°. After some hours the molten metal becomes coated with a film of oxide, but does not burn till heated to 1500° or thereabouts.

The standard electrode potential of tin is −0·14 volt; it dissolves fairly readily in acids to form stannous solutions. With dilute hydrochloric and sulphuric acids the action is slow, but rapid with the concentrated acids. With dilute nitric acid the products are stannous and ammonium nitrates. With stronger acid the stannous nitrate is oxidized to hydrated stannic oxide, and with very concentrated acid a protecting layer of this substance is formed immediately and very little action takes place. Tin dissolves slowly in boiling solutions of the alkalis, forming stannates and liberating hydrogen:

$$Sn + 2OH' + H_2O = SnO_3'' + 2H_2 \uparrow.$$
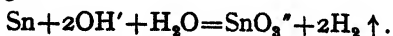
TIN COMPOUNDS.—Tin has two valencies, two and four, of which the latter is rather more stable, as the stannous compounds are fairly strong reducing agents, at any rate in solution. This is an important difference between tin and lead. While the stannous compounds are salt-like in character the stannic compounds are largely covalent, though in water the hydrated stannic ion can exist. The acidity of the amphoteric stannous hydroxide, $Sn(OH)_2$, is intermediate between that of the distinctly acidic germanous hydroxide and the feeble acidity of plumbous hydroxide, in which basic properties predominate.

Hydrides.—*Tin hydride*, SnH_4, is an unstable gas which can be prepared in poor yield by cathodic reduction of tin solutions. The gas is very easily dissociated.

Oxides and hydroxides.—*Stannous hydroxide*, $Sn(OH)_2$, is obtained as a white precipitate by the action of alkalis on stannous solutions. If the solution is boiled the hydroxide loses water and is converted to black crystalline stannous oxide, SnO, which can also be obtained by heating the dry hydroxide in the absence of air. When heated in air stannous oxide evolves heat and is converted to stannic oxide; at a red heat it will reduce steam. The oxide and hydroxide are insoluble in water and ammonia solution, but will dissolve in acids to form stannous salts or in alkalis to form stannites:

$$SnO + 2OH' = SnO_2'' + H_2O.$$
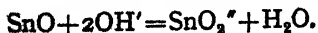
If the alkali is very concentrated a stannate and tin are slowly formed:

$$2SnO + 2OH' = SnO_3'' + Sn \downarrow + H_2O.$$
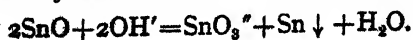
As might be expected, the stannites are reducing agents; they are known only in solution. The solutions absorb oxygen from the air to form stannates:

$$2SnO_2'' + O_2 = 2SnO_3'',$$
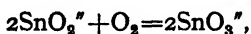
and if they are boiled, tin is precipitated and a stannate remains in solution:

$$2SnO_2'' + H_2O = SnO_3'' + Sn\downarrow + 2OH'.$$

Stannic oxide, SnO_2, associated with varying amounts of water, is obtained as a white precipitate when stannic solutions are made alkaline, or by their spontaneous hydrolysis:

$$Sn^{····} + 2H_2O \rightleftharpoons SnO_2\downarrow + 4H^·,$$
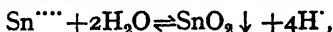
or by oxidizing tin with hot concentrated nitric acid. It is also precipitated when stannous solutions are exposed to the air:

$$2Sn^{··} + 2H_2O + O_2 = 2SnO_2\downarrow + 4H^·.$$
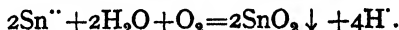
The anhydrous oxide can be made by burning tin in oxygen or air. In the finely-divided state it is used for making enamels opaque. The anhydrous oxide is insoluble in acids or alkalis, but on fusion with caustic alkalis or carbonates yields a soluble stannate:

$$SnO_2 + 2OH' = SnO_3'' + H_2O.$$
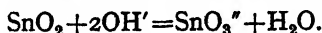
The product obtained from stannic solutions is more reactive than that formed by oxidizing tin with nitric acid, and it was formerly considered that 'stannic acid' could exist in allotropic forms. However, X-ray diffraction has failed to detect any essential difference between the products, which are both to be regarded as hydrated stannic oxide, no doubt with different particle size depending on the method of preparation. Stannate solutions are hydrolysed: even carbon dioxide will precipitate stannic oxide from them:

$$SnO_3'' + 2H^· = SnO_2\downarrow + H_2O.$$
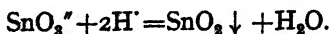
The stannates, which find use as mordants, occur in two series, exemplified by the salts $K_2Sn(OH)_6$ and K_2SnO_3.

Halides.—The hydrated stannous halides are ionic compounds with reducing properties, the stannic halides are covalent and are largely, if not entirely, hydrolysed by water. The action of the halogen on tin invariably produces the tetrahalide.

Stannous chloride, $SnCl_2$.—Solutions of this compound are made by dissolving tin in hot concentrated hydrochloric acid. If exposed to the air the solutions absorb oxygen and precipitate stannic oxide, and hydrolysis also takes place on evaporation to dryness, with the formation of stannous oxide. To prevent hydrolysis the

solution for use in the laboratory as a reducing agent is always kept acid. The first product of evaporation is the dihydrate $SnCl_2.2H_2O$, which under the name of *tin salt* is used as a mordant. The anhydrous chloride can be made by heating tin or stannous sulphide in hydrogen chloride gas:

$$Sn+2HCl=SnCl_2+H_2. \qquad SnS+2HCl=SnCl_2+H_2S.$$

The anhydrous salt melts at 245° and boils at 606° (compare the covalent tetrachloride), and the vapour density shows evidence of slight association.

Stannous chloride is extensively used as a reducing agent. It will reduce chromates to chromic salts and permanganates to manganous salts. With nitric acid hydroxylamine, NH_2OH, can be obtained; indeed, this is one of the methods of preparing hydroxylamine, but the conditions must be carefully controlled. Stannous chloride will precipitate mercury, silver, or gold from solutions of their salts (as in the preparation of purple of Cassius), but on the other hand can be reduced to metallic tin by such metals as zinc, aluminium, or even lead.

Solutions of stannous chloride for use in volumetric analysis must be kept under hydrogen to prevent atmospheric oxidation: for this reason they are not often used. When stannous chloride is used as a reducing agent stannic chloride is produced. In the presence of a sufficient concentration of hydrochloric acid it will remain in solution, but is otherwise hydrolysed and precipitated as dioxide or oxychloride.

Stannic chloride, $SnCl_4$, is prepared by burning tin in chlorine. If the metal is finely divided or in the form of foil the action takes place spontaneously. It can also be prepared by heating stannic oxide in carbon tetrachloride vapour (compare titanium, zirconium, etc.). It is a colourless liquid, freezing at −33° and boiling at 114°. Its volatility, solubility in organic solvents, and negligible electrical conductivity all point to a covalent character. On the other hand its aqueous solutions contain some chlorine ions, and the compound appears to ionize by combination with water:

$$SnCl_4+5H_2O \rightleftharpoons (Sn.5H_2O)^{\cdots\cdot}+4Cl'.$$
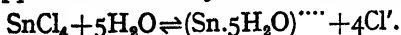
The increase of size by hydration stabilizes the stannic ion (p. 341).

The hydrolysis of stannic chloride is slow and reversible: it yields stannic oxide and hydrogen chloride:

$$SnCl_4+2H_2O \rightleftharpoons SnO_2\downarrow +4HCl.$$

The addition of hydrochloric acid to the solution reduces the hydrolysis not only by reason of its acidity but also by forming complex ions:

$$SnCl_4+2Cl' \rightleftharpoons SnCl_6.''$$

Ammonium chlorostannate, $(NH_4)_2SnCl_6$, was once used as a mordant for madder dyes under the name of *pink salt*. The fuming of stannic chloride in moist air is due to hydrolysis.

Stannous iodide, SnI_2, is only slightly soluble in water and is precipitated as a yellowish-red substance when iodide and stannous solutions are mixed. It melts at 320°.

Stannic iodide, SnI_4, obtained from tin and iodine, which combine with vigour, melts at 144° and boils at 340°. It is soluble in organic liquids and hydrolysed by water.

Sulphides.—*Stannous sulphide*, SnS, is a dark brown or black precipitate obtained by the action of hydrogen sulphide on stannous solutions, or by heating tin and sulphur.

Stannic sulphide, SnS_2, cannot be obtained by the action of sulphur on tin, as this reaction produces the stannous compound, but can be made by heating a mixture of tin and sulphur with ammonium chloride. If heated too strongly it decomposes into stannous sulphide and sulphur. It is a bright yellow compound, formerly much used in the preparation of gold paint under the name of ' mosaic gold.' It can be sublimed without decomposition.

Thiostannates.—When stannous sulphide is treated with a concentrated sulphide solution it dissolves to form a thiostannate, and tin remains. This may be compared with the action of concentrated alkalis on stannous oxide:

$$2SnS + S'' = SnS_3'' + Sn \downarrow .$$
$$2SnO + 2OH' = SnO_3'' + Sn \downarrow + H_2O.$$
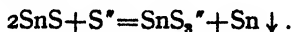
Stannous sulphide is completely soluble in ammonium polysulphide, with which it forms a thiostannate and other products:

$$SnS + S_2'' = SnS_3''.$$
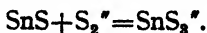
The same substance is produced when stannic sulphide dissolves in sulphide solutions:
$$SnS_2 + S'' = SnS_3''$$
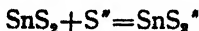
The solubility of stannous sulphide in polysulphide solutions is the basis of one method of separating tin from related elements. Stannic sulphide is reprecipitated from thiostannate solutions by the addition of acids:

$$SnS_3'' + 2H' = SnS_2 \downarrow + H_2S \uparrow .$$
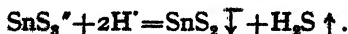
Sulphates.—*Stannous sulphate*, $SnSO_4$, is obtained in solution by dissolving tin or stannous hydroxide in sulphuric acid, and in the free state by evaporating the solution under reduced pressure. The solution is hydrolysed, and readily deposits basic salts.

Stannic sulphate is not known in the free state. Certain hydrated forms of stannic oxide can be made to dissolve in sulphuric acid, and by evaporation of the solution the dihydrate $Sn(SO_4)_2.2H_2O$,

or perhaps $H_2[SnO.(SO_4)_2]$, is obtained. It is soluble in water, but the solutions soon deposit stannic oxide.

Nitrates.—Neither stannous nor stannic nitrate can be obtained free from water of crystallization. If the hydrates are heated, hydrolysis takes place and oxides of nitrogen are evolved.

LEAD

Pb=207·21. *Atomic Number, 82*

History.—Lead has been known from very early times, and was called *plumbum nigrum* by the Romans to distinguish it from *plumbum candidum*, tin. The lead mines of Britain were worked as early as the first century A.D., and lead coffins of Saxon age have been discovered. Among the alchemists, lead was regarded as an imperfect metal—composed of an earthy sulphur and an undigested mercury—and was known as Saturn, on account of its supposed sympathy with the qualities of the celestial Saturn.

Occurrence.—Though not abundant, lead occurs in many different parts of the world, chiefly as galena, an impure form of lead sulphide, PbS, though sometimes as the oxide or carbonate. It is often associated with silver, and silver is recovered from lead residues (p. 468).

The United States, Mexico, and Spain are, in that order, the world's principal producers of lead. Many mines previously worked in England and Wales have long been abandoned, and the disused workings are familiar features of the countryside in parts of Yorkshire and other counties of the north and west.

Extraction.—Galena is roasted until the lead sulphide has all been converted to lead oxide or lead sulphate. The resulting mixture is then heated with more galena in a restricted supply of air, and sulphur dioxide is given off, leaving lead, which collects at the bottom of the furnace in the molten state and is run off:

$$PbS+2PbO=3Pb+SO_2 \uparrow \quad and \quad PbS+PbSO_4=2Pb+2SO_2 \uparrow .$$
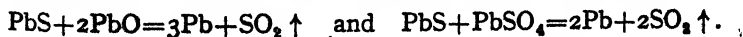
In a modification of the process, the roasting of the galena is made to yield principally the oxide, which is then reduced with coal: the slag from the first process is sometimes treated in this way.

Properties.—Lead is a bluish-grey metal, lustrous when freshly cut, but rapidly tarnishing in the air. When quite pure it has no bluish tinge, and lead which has been distilled in a vacuum keeps its lustre indefinitely as long as air is not admitted. It is the densest of the common metals, and has a comparatively low melting-point (327°), not so low, however, as that of tin. It boils at about 1550°. It is soft and malleable, and can be rolled into thin sheets

*U

(lead foil) or squirted into piping. It can easily be obtained in the form of large crystals by electro-deposition or by slow cooling of the liquid. Lead will mark paper; 'lead' pencils, however, contain not lead but graphite.

Owing to the ease with which thick sheets of lead can be manipulated they are much used in roofing and in making cisterns and rain-water pipes. Lead is only superficially oxidized by air and water, but drinking-water must not be carried in lead pipes if it is below a certain degree of hardness, as it may then dissolve dangerous quantities of the metal. Lead is also used in sulphuric acid containers and in accumulators. The alloys of lead include solder, pewter, and the various type-metals; bullets are made from an alloy of lead and nickel. Lead oxide and lead carbonate are used in paints and glazes, and lead tetraethyl, $Pb(C_2H_5)_4$, is added to petrol as an 'anti-knock.'

LEAD COMPOUNDS.—Lead, like tin, has valencies of two and four, but in its bivalent compounds it is electrovalent, in its quadrivalent compounds usually covalent; there is no quadrivalent lead ion. Plumbous hydroxide is a stronger base than stannous hydroxide and a weaker acid, nevertheless solutions of lead salts have a feebly acid reaction from hydrolysis. The bivalent compounds of lead have no reducing properties. Lead also differs from tin in the insolubility of its halides and sulphate (but see stannous iodide), and in being rather more electropositive. It will displace tin from its solutions. The oxides of tin and lead are also very different, and lead dioxide is the least stable of the dioxides of all the Group IV elements; it is a strong oxidizing agent.

Lead compounds are poisonous, and when taken in minute doses remain in the body; lead is therefore a cumulative poison. Workers in lead mines and in factories where lead is used have in the past, and even in the present day, suffered much from lead-poisoning, but the prevalence of poisoning is now much reduced by the use of dust-collectors. For centuries lead oxide was used to remove the acidity of wine which had become sour, until in the seventeenth century the danger of the practice was recognized. MELLOR tells us that a cabman whose first glass of beer every morning at a public-house was drawn from that which had been standing in lead pipes overnight finally suffered from lead colic.

Lead is probably the only element, other than hydrogen, whose isotopes are known to be partially segregated in nature (p. 318).

Lead combines with the halogens less readily than does tin, and is then converted to bivalent compounds. It is scarcely affected by hydrochloric or sulphuric acids in the cold, but will readily reduce hot concentrated sulphuric acid to sulphur dioxide. It also dissolves readily in hot dilute nitric acid, yielding oxides of

nitrogen, nitrogen, and sometimes ammonium nitrate. With concentrated acid the action is less rapid, as a film of lead nitrate, insoluble in concentrated nitric acid, protects the metal from attack.

Lead hydride, PbH_4, has been obtained in minute yield by an electrolytic reduction process. It is a very unstable gas (b.p. $-13°$).

Oxides and hydroxides.—*Lead monoxide*, litharge, PbO. When an alkali is added to solutions of lead salts, white lead hydroxide, $Pb(OH)_2$, associated with varying amounts of water, is precipitated; on boiling the solution it loses water and is converted to the yellowish-red substance litharge, PbO. The oxide can also be made by the slow atmospheric oxidation of molten lead, or by heating lead nitrate:

$$2Pb(NO_3)_2 = 2PbO + 2N_2O_4 \uparrow + O_2 \uparrow.$$
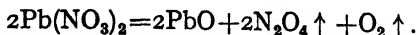
It is practically insoluble in water, but when moist has an alkaline reaction to litmus. It is readily soluble in acids, forming lead salts, and is also soluble in hot alkaline solutions in which plumbites might be supposed to exist:

$$PbO + 2OH' = PbO_2'' + H_2O.$$
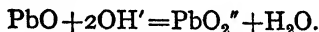
Although their existence in solution has commonly been assumed, it is remarkable that no examples of salts of supposed stannous or plumbous acids have yet been isolated. Formulae assigned to them are therefore speculative.

Lead sesquioxide, $Pb_2O_3.3H_2O$, is precipitated from solutions of lead salts by solutions of hypochlorites:

$$2Pb \cdot + 4OH' + ClO' = Pb_2O_3 \downarrow + Cl' + 2H_2O.$$
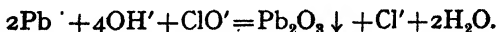
It is a yellow substance which in its behaviour with acids resembles a mixture of the monoxide and dioxide.

Triplumbic tetroxide, red lead, Pb_3O_4, is obtained by heating litharge in the air above $400°$, though the product of this process may not have the exact composition indicated by the formula. It is a bright red substance which occurs native in small quantities, and has long been used as a pigment. X-ray analysis proves it to be an association of PbO and PbO_2. It darkens on heating but regains its colour on cooling.

Lead dioxide, lead peroxide, PbO_2, is obtained from red lead and nitric acid ($Pb_3O_4 + 4H \cdot = 2Pb'' + PbO_2 \downarrow + 2H_2O$), or by the action of hydrogen peroxide on alkaline lead solutions, or by oxidizing with a halogen litharge suspended in dilute alkali. It can easily be prepared quantitatively by anodic oxidation of lead solutions. It is black or brown in colour and is insoluble in water.

It is a powerful oxidizing agent and is easily reduced by hydrogen on gentle heating, first to litharge and then to lead. On heating

with hydrogen chloride, in the free state or in solution, chlorine, plumbous chloride, and water are produced: with hot concentrated sulphuric acid, plumbous sulphate and oxygen. Lead dioxide reacts with easily oxidizable substances like sulphur, phosphorus, or sugar with incandescence or explosion.

Lead dioxide may be regarded as the anhydride of orthoplumbic acid, $H_2Pb(OH)_6$. It is only slightly soluble in alkaline solutions, but when fused with caustic potash forms a plumbate soluble in water,

$$PbO_2 + 2KOH = K_2PbO_3 + H_2O.$$
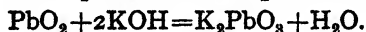
On dissolving the plumbate in concentrated alkali, and crystallizing by careful evaporation, the salt $K_2Pb(OH)_6$ is obtained, which at $110°$ reverts by the loss of water to the anhydro-plumbate K_2PbO_3 (cf. p. 604). The plumbates readily deposit lead dioxide formed by hydrolysis, and on heating lose oxygen.

The use of lead dioxide in accumulators has already been described (p. 269).

Lead carbonate, $PbCO_3$, occurs in nature as *lead-spar* or *cerussite*. Sodium carbonate precipitates a basic carbonate, *white lead*, $2PbCO_3.PbO.H_2O$, from lead solutions, and to obtain the normal carbonate a less alkaline solution must be used; a solution of sodium bicarbonate is suitable:

$$Pb^{..} + 2HCO_3' = PbCO_3 \downarrow + H_2O + CO_2.$$

White lead is of great commercial importance and when ground up with oil is used as a paint. The object of the various processes for making it is to reduce the size of the particles as much as possible. Metallic lead is exposed to the action of acetic acid vapour and carbon dioxide. The function of the acetic acid is probably to get the lead into solution without decomposing the basic carbonate. In the modern chamber process the lead is suspended in sheets from the ceiling of a chamber, kept at $70°$, into which the mixed gases are admitted. After two months the whole of the metal has been converted to white lead. A better-quality white lead is made by the long-established Dutch process. A little dilute acetic acid is placed in earthenware pots, which are covered with perforated lead sheets and piled in stacks with decaying tan between them. The fermentation of the tan produces heat and carbon dioxide, and after three or four months the process is complete. The product of either process is crushed and ground. Electrolytic processes are also used.

White lead paint has two serious defects: it is poisonous, and in the air of towns, which contains hydrogen sulphide, it blackens owing to the formation of black lead sulphide.

Halides.—Lead forms stable bivalent halides which are ordinary salts. They are only sparingly soluble in water, and are much more

soluble in hot water than in cold. Lead tetrachloride, an unstable yellow liquid, is the only certainly known tetrahalide of lead. The tetrabromide and tetraiodide could not exist, owing to the high oxidizing potential of quadrivalent lead (Pb^{4+}/Pb^{2+}=ca.-1.7 v.).

Plumbous fluoride, PbF_2, is obtained as a colourless precipitate from a lead solution and a soluble fluoride.

Plumbic fluoride, PbF_4, has not been isolated, but the yellow anion PbF_6'' can be obtained in solution by the action of very concentrated hydrofluoric acid on lead dioxide:

$$PbO_2 + 6HF \rightleftharpoons PbF_6'' + 2H_2O + 2H^{\cdot}.$$
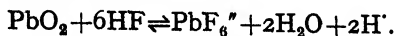
The action is reversible, and on adding water to the solution the dioxide is precipitated. By dissolving sodium plumbate, Na_2PbO_3, in hydrofluoric acid a stable sodium fluoplumbate, Na_2PbF_6, can be obtained: compare the analogous compounds of silicon, titanium, and tin.

$$PbO_3'' + 6HF = PbF_6'' + 3H_2O.$$
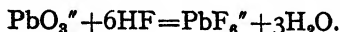
Compounds of quadrivalent lead appear to be stabilized when the lead can complete a covalency of six.

Plumbous chloride, $PbCl_2$, is obtained from hydrochloric acid and the oxide or carbonate, or by precipitating a lead solution with a soluble chloride. It is a colourless compound and can be recrystallized from boiling water. One hundred grams of water dissolve 3.3 grams at $100°$ and 0.7 gram at $0°$.

Plumbic chloride, $PbCl_4$, is best prepared from the stable salt ammonium chloroplumbate, $(NH_4)_2PbCl_6$, which is obtained as a yellow precipitate by adding ammonium chloride to a cold solution of lead dioxide in concentrated hydrochloric acid:

$$PbO_2 + 4H^{\cdot} + 6Cl' = PbCl_6'' + 2H_2O.$$
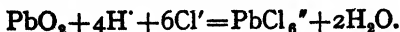
When the ammonium salt is treated with well-cooled concentrated sulphuric acid, lead tetrachloride separates as a yellow oily liquid freezing at $-15°$:

$$PbCl_6'' + 2H^{\cdot} = PbCl_4 + 2HCl \uparrow.$$
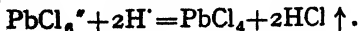
It is a non-conductor of electricity, is soluble in organic liquids, and is hydrolysed by water to form lead dioxide and hydrochloric acid:

$$PbCl_4 + 2H_2O = PbO_2 + 4HCl.$$
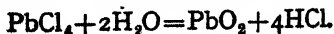
It readily decomposes into plumbous chloride and chlorine.

Plumbous bromide, $PbBr_2$, is obtained as a white precipitate by adding a soluble bromide to a lead solution. It is approximately as soluble as the chloride in cold water, but the solubility has a higher temperature-coefficient.

Plumbous iodide, PbI_2, differs from the other plumbous halides

in being bright yellow in colour and in being less soluble in water: it is prepared by similar methods.

Plumbous sulphate, $PbSO_4$, is a white substance almost insoluble in water. It occurs native as *anglesite* in Anglesey and elsewhere, having been produced by the oxidation of galena, PbS. It is prepared by the action of hot concentrated sulphuric acid on lead:

$$Pb+2H_2SO_4=PbSO_4\downarrow+SO_2\uparrow+2H_2O,$$

or, together with lead sulphide, by the action of sulphur dioxide on molten lead:

$$2Pb+2SO_2=PbSO_4+PbS,$$
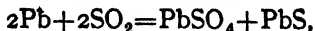
or by precipitating a lead solution with dilute sulphuric acid. It has been used as a paint, as it is neither so poisonous as white lead, nor so readily blackened by hydrogen sulphide.

Plumbic sulphate, $Pb(SO_4)_2$, is an unstable substance which has been prepared by anodic oxidation. It is hydrolysed by water.

Plumbous sulphide, PbS, occurs native as galena, and is precipitated as a brownish-black substance by hydrogen sulphide from lead solutions, but when prepared from lead and sulphur is grey. Its reactions with lead oxide and lead sulphate have already been described.

Lead nitrate, $Pb(NO_3)_2$, is the commonest soluble salt of lead. It is prepared from nitric acid and lead, lead oxide, or lead carbonate, and is a colourless compound very soluble in water. Its decomposition by heating has already been described.

Lead chromate, $PbCrO_4$, is a yellow precipitate obtained from chromate solutions and lead solutions. It is used as a pigment (' chrome yellow ').

Lead acetate, $Pb(CH_3.COO)_2.3H_2O$, is obtained from litharge and excess of acetic acid; from its sweet taste it is called ' sugar of lead.' Its solutions contain complex ions, probably of chelate structure, and all the slightly soluble compounds of lead are more soluble in acetate solutions than in pure water.

In the majority of its covalent compounds lead is quadrivalent; we may mention the *tetra-acetate,* $Pb(CH_3.COO)_4$, and *lead tetraethyl,* $Pb(C_2H_5)_4$.

Lead tetra-acetate, $Pb(CH_3CO_2)_4$, is obtained as colourless crystals by treating well-dried ' red lead,' Pb_3O_4, with anhydrous acetic acid at 60°. The compound is instantly hydrolysed by water to lead dioxide. Its solubility in organic solvents (benzene, chloroform) indicates that it is covalent. Some use is made of the compound as an oxidizing agent in organic chemistry.

CHAPTER XIX

GROUP V

[NITROGEN], PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH,
VANADIUM, NIOBIUM, TANTALUM

$$[N] - P \Big\langle \begin{matrix} V - Nb - Ta \\ As - Sb - Bi \end{matrix}$$
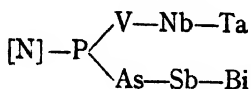
IN Groups V, VI, and VII the typical elements quite definitely resemble the B subgroup, while the metals of the A subgroups can be compared among themselves: they form the transition elements in the wider sense of the term.

Some of the properties of Group V elements are tabulated below:

	Typical		Subgroup B			Subgroup A		
	N	P	As	Sb	Bi	V	Nb	Ta
Atomic Number	7	15	33	51	83	23	41	73
Atomic Weight	14·008	30·975	74·91	121·76	209·0	50·95	92·9	180·9
Density	(at B.P. 0·81)	(a) 1·84	5·7	6·7	9·8	6	7·3	16·6
Atomic Volume	(17·3)	16·9	13·2	18·2	21·4	8·5	12·7	10·9
Melting-point	−210°		sublimes at 620°	630°	271°	1720°	1950°	3027°

THE GROUP V ELEMENTS

The elements from nitrogen to bismuth form a well-defined series in which a gradual change of properties is noticeable. Some of the more obvious variations may be mentioned.

The two end elements do not display allotropy, unless active nitrogen be included as an allotrope, but the middle elements do. The colourless or yellow form has a lower melting-point than the other allotropes and is less dense; it has a non-metallic appearance and will dissolve in carbon disulphide, whereas the behaviour of the metallic form is precisely the opposite. The stability of the non-metallic as compared with the metallic form decreases from phosphorus to bismuth.

As we pass from nitrogen, a typical non-metal, to bismuth, an element which is more metallic than otherwise, a gradual change is noticeable between these limits. Nitrogen, and to a less degree

phosphorus, are the only elements of the group whose hydrides are sufficiently stable to form bases. All the hydrides of the group belong to the non-metallic type (p. 363), and it is only to be expected that their stability should decrease together with the non-metallic character of the elements. Ammonia is a stable substance, phosphine is decomposed by heating, and the remaining hydrides decompose with increasing readiness in the cold.

The change in the metallic character of the element may be brought out by considering the oxides and the chlorides. The oxides of nitrogen and phosphorus are acidic, those of arsenic and antimony are amphoteric, and bismuth oxides are predominantly basic, while the increase in basic character is as usual accompanied by a decrease in volatility. The melting-points of the trioxides (or sesquioxides) and trichlorides are shown in the table:

	N	P	As	Sb	Bi
Sesquioxide	$-85°$	$23°$	$275°-315°$	$660°$	817
Trichloride	?	$-112°$	$-16°$	$73°$	$233°$

MELTING-POINTS OF TRIOXIDES AND TRICHLORIDES OF SOME GROUP V ELEMENTS

Evidences of saline character begin with arsenic chloride, which is stable in solution in concentrated hydrochloric acid. There is some evidence that the ion As⁣⃛ may exist in small concentration in such solutions, whereas nitrogen and phosphorus are incapable of forming cations. The first product of the hydrolysis of the trichlorides of antimony and bismuth is not the hydroxide, but the oxychloride SbOCl or BiOCl. Bismuth oxychloride is unaffected by boiling water, but antimony oxychloride can suffer further hydrolysis.

The valency shells of the atoms of these elements contain five electrons, but they all have the power of forming stable compounds in which they are tervalent. In these compounds the two unshared electrons may either exist as a lone pair, as in ammonia, or they may be altogether inert, as they appear to be in bismuth, which scarcely forms quinquevalent compounds. The covalency maximum of nitrogen is four, and the lone pair in its tervalent compounds gives them powerful donor properties (see ammonia). The tervalent compounds of phosphorus are also unmistakable donors, and phosphine resembles ammonia in its power of forming phosphonium halides. The only resemblance between Subgroup A, which consists of transition elements, and the rest of the group is in the quinquevalent compounds, and the properties of these substances (e.g. vanadates) are somewhat modified by the numerous lower valencies possible for the Subgroup A elements but not for the others, so

that the quinquevalent compounds of Subgroup A are oxidizing agents. As usual, throughout the group the fluorides more than any other compound display the elements in their maximum valency, and they all, except nitrogen, form pentafluorides. The Subgroup A elements are all typical metals with high melting-points and typical transitional properties, and in the elementary state or in their compounds of lower valency they bear not the slightest resemblance to the other elements of Group V.

PHOSPHORUS

P=30·975. *Atomic Number*, 15

History.—In 1677 a bailiff named BALDWIN, in Saxony, had prepared a substance (impure barium sulphide) which, after exposure to sunlight, shone in the dark; it was therefore called Baldwin's ' phosphorus.' About the same time (1669) an alchemist of Hamburg, named BRAND, prepared a substance (the modern yellow phosphorus) with similar properties but possessing the additional merit of shining in the dark without previous exposure to sunlight. His method was to distil a mixture of concentrated and fermented urine with sand, when the phosphorus was obtained, as a blackish solid. KUNCKEL, a German chemist of note, after vainly trying to purchase the secret from Brand (who had already sold it to an adventurer named KRAFFT), hit upon the same method of preparation independently in 1678. Krafft exhibited the element in England, where it excited the curiosity of chemists, and BOYLE (1680) made a third independent discovery of its extraction from urine. Boyle published the details of his process and hence for many years phosphorus was known as ' English phosphorus.'

In 1769–70, GAHN showed that phosphorus is present in bones, an observation confirmed by SCHEELE in 1771, who also devised a method of preparing it from bone-ash. LAVOISIER (1772), from a study of its behaviour on combustion, concluded that it was an element.

Occurrence and Extraction.—Phosphorus is an abundant element and almost invariably occurs as a phosphate; phosphates are very widely distributed over the earth. The element in one form or another appears to be essential to the life of animals and plants, and some four or five pounds of calcium phosphate, $Ca_3(PO_4)_2$, are contained in the skeleton of a grown man. Guano, the dried excrement of sea-birds, contains a considerable proportion of phosphates derived from the fish on which these birds feed. The

conversion of calcium phosphate into the so-called calcium super-phosphate, to be used as a fertilizer, is now an important industry (p. 500).

Until the beginning of the present century, the phosphorus of commerce was obtained from the calcium phosphate contained in bone-ash, which, after conversion to calcium hydrogen phosphate with sulphuric acid, was ignited till the metaphosphate remained:

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2H_2O \uparrow .$$
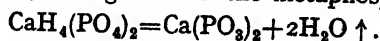
This substance was then distilled with charcoal:

$$3Ca(PO_3)_2 + 10C = Ca_3(PO_4)_2 + P_4 \uparrow + 10CO \uparrow ,$$

and the phosphorus was condensed under water. The process is very wasteful, and since the development of the electric furnace is of small commercial importance.

The arrangement of a phosphorus furnace can be seen from the diagram. The charge consists of phosphorite (impure calcium phosphate) mixed with coke and sand, added to secure a liquid slag. It is admitted at C, and current is passed between the electrodes AA, thus providing sufficient heat for the reaction:

FIG. 128. PHOSPHORUS FURNACE
(DIAGRAMMATIC)

$$2Ca_3(PO_4)_2 + 10C + 6SiO_2 = P_4 \uparrow + 10CO \uparrow + 6CaSiO_3.$$
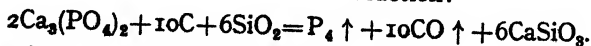
At the end of the operation the slag is run out at D. The phosphorus fumes are condensed under water, and in one modification of the process the whole plant is filled with coal-gas or carbon monoxide during the operation. Nine kilowatt-hours are required per kilogram of phosphorus. The carbon monoxide produced in phosphorus manufacture is used to make hydrogen from steam, and in the Liljenroth process hydrogen is produced from phosphorus vapour and steam on the surface of a catalyst:

$$2P + 8H_2O = 2H_3PO_4 + 5H_2.$$
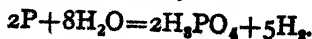
If alumina is used instead of quartz in the phosphorus furnace, the slag can be used as cement.

The total annual production of phosphorus is between thirty and forty thousand tons.

The Allotropy of Phosphorus.—Phosphorus prepared by the modern electric processes is nearly 100 per cent pure, but may contain traces of arsenic. It can be obtained perfectly pure by distilling the commercial product in steam in an apparatus from which the air has been driven by a current of carbon dioxide, which should be kept up during the distillation. Phosphorus spontaneously oxidizes in the air, and must therefore be kept under water.

The element exists in three principal forms, colourless (' yellow '), red and black, and as there are two modifications of colourless phosphorus, distinguished by the letters α- and β-, the total number of allotropes is four. Many other varieties have been reported, but they are mostly distinguished from red phosphorus only by a difference in the state of division or by the presence of impurities. A fifth variety, HITTORF's violet or 'metallic' phosphorus, is considered by some to consist of coarse grains of red phosphorus, while others are of the opinion—and this is perhaps the likelier view — that violet phosphorus is a true allotrope and red phosphorus merely a solid solution of the colourless and violet forms in equilibrium.

Colourless phosphorus, the form commonly met with in the laboratory, is a solid of density 1·84, melting at 44° and boiling at 287°. It darkens on exposure to light, and unless prepared in a darkened room has a distinct yellow colour which gives it its usual name of ' yellow phosphorus.' This yellow colour can be removed by oxidizing agents such as dilute chlorine water. The ordinary or α-form of colourless phosphorus crystallizes in the cubic system, but in 1914 BRIDGMAN noticed that if it was cooled to a very low temperature and allowed to grow warmer a definite irregularity occurred in the heating curve at −77°. The variety stable below this temperature is called the β-form: it can be produced from the α-form at ordinary temperatures by the application of pressure—about 11 metric tons per sq. cm. at 60°.

Colourless phosphorus is insoluble in water, but it will dissolve in about four parts by weight of carbon disulphide, and solutions in benzene, chloroform, and other organic solvents can also be prepared, as well as in the liquid compound phosphorus tribromide. The solutions in organic solvents do not conduct electricity, and the phosphorus is in the form of P_4 molecules.

Red phosphorus, though formerly described as amorphous, is a mass of rhombohedral crystals. It is soluble in alcoholic potash, but not in the organic solvents that dissolve the yellow variety. Its physical properties, among them the colour, heat of combustion, specific gravity (2·05 to 2·39), and melting-point (under pressure), depend on the method and temperature of its preparation, and

many substances have been reported as allotropes which differ from it only in physical properties.

At ordinary temperatures colourless phosphorus has a higher vapour pressure than red phosphorus and is consequently unstable. The rate of transformation is negligible, but it increases on heating, and is also accelerated by light, pressure, or the electric discharge, or such catalysts as iodine or selenium. It proceeds smoothly at 250° in the absence of catalysts, and is carried out at this temperature on an industrial scale. Any unchanged residue can be removed from the product by boiling with aqueous caustic soda, which reacts with colourless but not with red phosphorus (see phosphine, p. 620).

There is no transition-point between colourless and red phosphorus at atmospheric pressure, because the red variety volatilizes without melting: colourless phosphorus is formed by condensation of the vapour. The change readily takes place at 350°. From the curves connecting vapour pressure with temperature it appears that red and colourless phosphorus would be in equilibrium with the liquid at 43 atmospheres and 590° (the triple point). No difference can be detected in the vapour from the various allotropes, which all have a density corresponding with a molecule P_4. The heat of combustion of colourless phosphorus is rather higher than that of the red form, so that heat will be evolved in the transformation of yellow to red, and the stability of the red form will diminish with rising temperature, as the facts show.

Hittorf's ' metallic ' or *violet phosphorus*, a form very similar to the red variety, is prepared by cooling a solution of phosphorus in molten lead which has been maintained for a day or two at 800°, and removing the lead from the violet rhombohedral crystals. This variety differs from red phosphorus only in the melting-point (620°–625°) and in the development and size of the crystals, and is believed to consist of red phosphorus in a coarsely-grained condition. When a solution of colourless phosphorus in the tribromide is kept at 180°, a third red variety, SCHENCK's *scarlet phosphorus*, is slowly precipitated. As might be expected from its method of preparation, it is red phosphorus in a fine state of subdivision. Colloidal solutions of both red and colourless phosphorus can be prepared. By applying a pressure of 12 metric tons per sq. cm. to colourless phosphorus at 200° Bridgman was able to prepare a new allotrope known as *black phosphorus*, with a density of 2·69. It is otherwise very like the red variety, but is a better conductor of heat and electricity.

General Properties.—Phosphorus is a reactive element which shows a pronounced tendency to unite with atmospheric oxygen. In the open air the spontaneous oxidation of the colourless variety

of the element raises its temperature until it bursts into flame. The ignition temperature is low, and it is unsafe to hold phosphorus in the fingers, while in the presence of finely-divided and easily oxidizable substances, such as charcoal, phosphorus may ignite at room temperature. In a well-known experiment a filter-paper is impregnated with a solution of phosphorus in carbon disulphide. The solvent quickly evaporates and leaves the phosphorus in a very finely-divided condition. The filter-paper first emits fumes of oxide and then takes fire.

It has been known for centuries that the spontaneous oxidation of phosphorus is attended by luminosity, but in spite of laborious research the phenomenon is still only incompletely understood. The most remarkable feature of the luminosity is the effect of pressure, for it is found that reducing the pressure increases the glow, whereas the contrary might have been expected. The glow will not take place in neutral gases or in high vacua, and is therefore closely connected with the oxidation process; it is not greatly affected by oxygen pressure within the limits 100–500 mm. of mercury, but is much reduced by smaller or greater pressures. Intensive drying reduces the glow without altogether arresting it, but the glow can be poisoned by the addition of very small quantities of various vapours, e.g. that of turpentine. The glow is accompanied by the production of ozone and by the ionization of the surrounding air or oxygen, which will discharge an electroscope. Very small quantities of phosphorus are sufficient to produce these effects. Thus, if water containing a very little phosphorus is boiled, the vapour is easily visible in the dark (this is MITSCHERLICH'S test for phosphorus).

The free combustion of phosphorus in a plentiful supply of air or oxygen produces white clouds of the pentoxide, but if the supply of air is restricted lower oxides are also produced. Phosphorus will not combine directly with gaseous hydrogen, and is scarcely affected by cold water, in which it is almost insoluble, though the water under which phosphorus is preserved always has a disagreeable smell of phosphine. Phosphorus reacts violently with all the halogens at room temperature. It is very easily oxidized, and oxidation sometimes takes place with explosive violence, e.g. the reaction with potassium chlorate. In the presence of water the oxidation of phosphorus produces phosphoric acid. Phosphorus will also combine with many metals forming phosphides, and with sulphur to form sulphides of phosphorus. Colourless phosphorus, but not the red variety, dissolves in aqueous alkalis, forming phosphine and other substances. It is not affected by acids as such, but various reactions may take place on heating: thus hot concentrated sulphuric acid is reduced to sulphur dioxide.

Phosphorus is sometimes used in the laboratory as a reducing agent; thus FARADAY used it to prepare colloidal solutions of gold from gold salts. It will also precipitate copper and silver from solutions of their salts, and a stick of phosphorus immersed in a solution of copper sulphate becomes red from a coating of the metal; but other substances are produced as well.

Although phosphorus in the form of phosphates is essential to life, yet the element itself, in the colourless form at least, is very poisonous. Colourless phosphorus was formerly used in the manufacture of matches, and the health of the workmen suffered severely from the phosphorus vapour in the air, until the manufacture of these matches was made illegal. The red form which is now used is harmless.

The addition of copper phosphide to certain alloys increases their strength: the best-known phosphorus-containing alloys are the *phosphor bronzes*. The most important use of phosphorus is, however, the manufacture of matches. The modern safety-match is an aspen stick tipped with a mixture of sulphur and potassium chlorate, and is ignited by rubbing on a surface coated with red phosphorus and antimony sulphide. Other matches are tipped with a mixture of the sulphides of phosphorus, chiefly P_4S_3, with potassium chlorate.

PHOSPHORUS HYDRIDES.—The principal hydride of phosphorus has the formula PH_3, and is called **phosphine**. It is most easily prepared by boiling colourless phosphorus with aqueous alkali in an apparatus from which the air has been excluded. The gas thus obtained is spontaneously inflammable in air, but the inflammability can be destroyed by passing it through concentrated sulphuric acid or by other methods, and is due to the presence of certain other hydrides of phosphorus. The product of this process also contains at least 50 per cent of hydrogen. An approximate equation is:

$$4P + 5OH' + 3H_2O = PH_3 \uparrow + 2H_2 \uparrow + H_2PO_2' + 2HPO_3''.$$
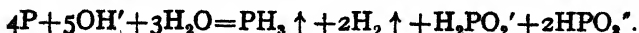
Pure phosphine can be obtained by the action of water on phosphonium iodide: $$PH_4I = PH_3 \uparrow + HI;$$

a little alkali is added to the water to retain the hydrogen iodide.

Phosphine is a colourless gas with a disgusting smell; perhaps the nastiest of all inorganic odours. It can be condensed to a liquid at —87° and to a solid at —133°. It is slightly soluble in water, but the solution is unstable and yields hydrogen and phosphoric acid. Pure phosphine is not spontaneously inflammable in air, but it may ignite or explode when mixed with oxygen, and rarefaction of the mixture can always be made to bring about this result at ordinary temperatures. The spontaneous ignition of impure

phosphine has been suggested as the cause of the ' will-o'-the-wisp ' sometimes seen over marshy ground, the phosphine having been produced by the decomposition of animal matter.

Phosphine is an unstable substance easily decomposed into its elements by heat. The decomposition is of the first order, but it takes place on the walls of the containing vessel. Phosphine is also decomposed by the halogens, which form halides of phosphorus and of hydrogen, and by sulphur, which forms sulphides. It is absorbed by solutions of the salts of silver and gold (and other metals), with the production of precipitates of varying composition; with the solutions named both the metal and phosphides are formed. Phosphine will also react under certain conditions with the halogen hydrides to form the phosphonium compounds, analogous to the ammonium salts:

$$PH_3 + HI = PH_4I.$$
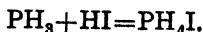
The reaction with hydrogen iodide takes place under ordinary conditions when the gases are mixed, but phosphonium bromide must be made in solution in some inert solvent, and to prepare phosphonium chloride it is necessary to compress the reaction mixture strongly and to cool it.

Phosphonium iodide, PH_4I, is commonly prepared by the action of a little water on phosphorus tri-iodide. Phosphorus is dissolved in carbon disulphide, iodine is added to it, and the solvent is distilled off while air is kept from the apparatus by a current of carbon dioxide. Water is then added, and after the heat of the reaction has abated the mixture is warmed in order that the whole of the phosphonium iodide may sublime into a wide tube fitted to receive it. The whole action may be represented:

$$9P + 5I + 16H_2O = 5PH_4I \uparrow + 4H_3PO_4.$$
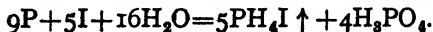
Phosphonium iodide is a colourless crystalline solid. On heating, it readily decomposes into phosphine and hydrogen iodide, and from these substances some hydrogen and phosphorus tri-iodide may be obtained. With water it quickly yields phosphine and hydrogen iodide and is very readily decomposed by oxidizing agents of all kinds.

Phosphonium bromide, PH_4Br, is a colourless solid which dissociates at a lower temperature than phosphonium iodide, and *phosphonium chloride*, PH_4Cl, cannot exist at ordinary temperatures and pressures.

Liquid hydrogen phosphide, P_2H_4, is the spontaneously inflammable ingredient of the mixed hydrogen phosphides prepared by the action of caustic alkalis on phosphorus. It is made by the action of excess of water on calcium phosphide, Ca_3P_2, and is evolved

from the reaction mixture, which is kept at 60°, as a gas which can be condensed to a liquid by ice-water. The whole of the apparatus must be filled with hydrogen. It is an unstable, colourless liquid with a low boiling-point, and is spontaneously inflammable in the air. The products of combustion form a thick white cloud which contains water and oxyacids of phosphorus. Liquid hydrogen phosphide is insoluble in water.

'Solid hydrogen phosphide' is a yellow solid which accompanies the liquid hydrogen phosphide produced by the action of water on calcium phosphide. It can be prepared, though in very small yield, by passing the gaseous products of this reaction through calcium chloride, which decomposes the liquid phosphide P_2H_4 into gaseous phosphine and the solid phosphide. It is recovered by dissolving the calcium chloride in cold dilute hydrochloric acid and filtering off the solid residue. It is a yellow solid with no smell, quickly decomposed by moist air in the light and less quickly in the dark; it is also decomposed by water, with which it forms hydrogen and phosphoric acid.

Its empirical formula approximates to P_2H, although the composition is somewhat variable. A molecular weight determination in which white phosphorus was used as solvent suggested a molecular formula $P_{12}H_6$, but the solid yields no definite X-ray diffraction pattern, and is now considered to be amorphous phosphorus containing dissolved (or adsorbed) phosphine.

Phosphides of the Metals.—Our knowledge of these compounds is not very extensive. Phosphorus combines with most of the metals if heated with them, and some phosphides have been made by the reduction of phosphates, as for instance with carbon in the electric furnace. When phosphine is passed through salt solutions phosphides are sometimes precipitated, often together with the metal. Most phosphides are decomposed by water, with the liberation of phosphine, but some few, such as copper phosphide, are stable enough to be used in small proportions in alloys. The *alkali-metal phosphides* are made by direct combination, as is aluminium phosphide, AlP, which in reaction with acids provides a convenient source of pure phosphine.

Calcium phosphide, Ca_3P_2, can be made by direct combination, but is more often prepared from calcium carbide and phosphoric oxide, or by heating calcium phosphate with carbon in the electric furnace. It is a brown crystalline refractory substance, stable in the air but readily decomposed by water, with which it liberates hydrogen and liquid hydrogen phosphide together with some solid hydrogen phosphide. If air is present these substances take fire with the production of clouds of phosphoric acid, and calcium phosphide is used in the production of smoke-screens at sea.

OXIDES.—The principal oxides of phosphorus are phosphorous oxide, P_4O_6, phosphorus tetroxide, $(PO_2)_n$, and phosphoric oxide, P_2O_5.

Phosphorous oxide, P_4O_6, sometimes called *phosphorus trioxide* from the empirical formula P_2O_3, is obtained by the combustion of phosphorus in an insufficient supply of air. As some of the pentoxide is always produced at the same time, and as phosphorus is appreciably volatile at the temperature at which the combustion is carried out, the conditions must be carefully regulated if contamination of the product is to be avoided. A slow stream of air is aspirated from left to right through the apparatus shown in the diagram while the phosphorus is gently warmed. Any unburned
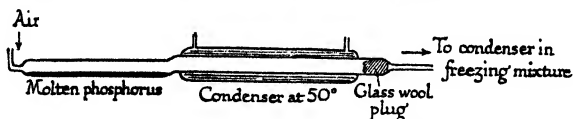
FIG. 129. COMBUSTION OF PHOSPHORUS TO FORM PHOSPHOROUS OXIDE

phosphorus is condensed by the water-jacket, which is kept at 50° or slightly over, while the plug of glass wool catches any pentoxide. The trioxide, however, is carried into a condenser cooled in a freezing-mixture, where it collects as a colourless solid; it is best to interrupt the air current before the whole of the phosphorus has been consumed. The trioxide is freed from traces of phosphorus by fractional crystallization from carbon disulphide, followed by distillation.

Phosphorous oxide is a crystalline substance melting at 23° and boiling at 173°; it has a peculiar odour. The vapour density corresponds with the formula P_4O_6. When strongly heated in the absence of air, it yields phosphorus and phosphorus tetroxide:

$$2P_4O_6 = 3P_2O_4 + 2P,$$
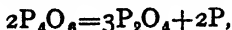
but it combines with oxygen from the air at all temperatures, forming either the tetroxide or the pentoxide, according to the conditions. When it is gently warmed in oxygen the reaction is violent and even explosive. With cold water the oxide slowly dissolves to form phosphorous acid:

$$P_4O_6 + 6H_2O = 4H_3PO_3,$$

but with hot water the reaction is vigorous, phosphorus is deposited, and phosphorus hydrides and phosphoric acid are produced.

Phosphorus tetroxide, empirical formula PO_2, is so called because the empirical formula is intermediate between those of the trioxide P_2O_3 and the pentoxide P_2O_5, or possibly by analogy with nitrogen

tetroxide, but it is probably best represented by P_4O_8. It is prepared, as already described, by heating phosphorous oxide in a vacuum to nearly 300°, and then sublimes into the cool parts of the apparatus.   It is also present in the mixture of oxides obtained by the combustion of phosphorus in a limited supply of air.   It is a colourless crystalline substance which deliquesces in the air and can be sublimed without change at about 180°.   It is soluble in water, but the solution does not contain hypophosphoric acid, $H_4P_2O_6$, as might be expected, but behaves rather as a mixture of metaphosphoric and phosphorous acids:

$$2PO_2 + 2H_2O = HPO_3 + H_3PO_3.$$
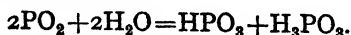
Phosphorus pentoxide, P_4O_{10}, the best-known and most familiar oxide of phosphorus, is obtained by burning phosphorus in a liberal supply of air or oxygen.   When carried out under these conditions the combustion of phosphorus yields a white and singularly brilliant flame.   The commercial product usually contains lower oxides and sometimes elementary phosphorus; and is purified by sublimation in a stream of oxygen over platinized asbestos, which catalyses the complete oxidation of these substances.

FIG. 130.   PHOSPHORUS PENTOXIDE DRYING-TUBE FOR GASES

Phosphorus pentoxide is a white powder which can be obtained in several crystalline forms.   The most volatile, or α-form, consists of molecules P_4O_{10}.   It can be sublimed without difficulty at 250°.   Other less volatile forms are macromolecular and contain PO_4 tetrahedra mutually linked by three of the oxygen atoms.   The pentoxide in the α-form has an affinity for water exceeding that of any known substance, and is chiefly used for withdrawing water or its elements from other substances, the product of the reaction being the very stable metaphosphoric acid.   For this reason phosphorus pentoxide becomes sticky and pasty if exposed to the atmosphere even for short periods, and its use as a desiccating agent is inconvenient, since it is very liable to clog the apparatus.   It is consequently used only when a high degree of desiccation is required, and is then commonly protected by calcium chloride or sulphuric acid driers from the access of considerable quantities of water.   The diagram shows the commonest form of drying-tube for gases.   The wide tube is sealed off at A after the oxide has been put

in. For most experiments on intensive drying the use of this substance is essential. The oxide is much used in the preparation of acid anhydrides; with nitric and perchloric acids it yields nitrogen pentoxide and chlorine heptoxide, and with sulphuric acid sulphur trioxide. It is also extensively used in organic chemistry.

THE OXYACIDS OF PHOSPHORUS.—The types of these acids are:

Hypophosphorous acid:	H_3PO_2	$PO(OH)H_2$
Phosphorous acid:	H_3PO_3	$PO(OH)_2H$
Hypophosphoric acid:	$H_4P_2O_6$	$PO(OH)_2$
		$\|$
		$PO(OH)_2$
Phosphoric acid:	H_3PO_4	$PO(OH)_3$
Perphosphoric acid:	H_3PO_5	$PO(OH)_2.O.OH$

It will be noticed that with the exception of hypophosphoric acid these form a sequence in which each has the formula H_3PO_n, but the table shows only the simplest type of each acid, and most of them exist in several condensed forms, which will be discussed under the appropriate headings. The structural formulae given are largely established, and they help to make the relations between the acids clearer than they otherwise would be.

Hypophosphorous acid, H_3PO_2.—The solution remaining after the preparation of phosphine from phosphorus and caustic alkali contains a hypophosphite. If the preparation of this compound is the object of the experiment, baryta is used instead of caustic soda, and the liquid afterwards neutralized by passing carbon dioxide through it. This precipitates barium carbonate, which can be filtered off, and barium hypophosphite can be obtained by evaporating the liquid. By treating a solution of this substance with dilute sulphuric acid a solution of hypophosphorous acid is obtained, from which nearly all the water can be driven by very cautious evaporation, which may with advantage be carried out under reduced pressure.

Hypophosphorous acid is a colourless crystalline solid which melts in the neighbourhood of 25°. It is very soluble in water, and the solution behaves as a fairly strong monobasic acid. There is a mass of evidence for this conclusion—titration, conductivity, hydrogen ion concentration, and so on—and since acid properties are usually assigned to hydroxylic hydrogen, the formula of the acid is supposed to be $H{\overset{HO}{\underset{H}{\Big>}}}P{=}O$. When hypophosphites are dissolved in water containing deuterium oxide, they are found upon

recovery to contain no deuterium. It is certain that if the anion contained a hydroxyl group exchange between hydrogen and deuterium would rapidly occur. The anion is therefore H_2PO_2' and not $HP(OH).O'$.

Hypophosphorous acid and the hypophosphites are powerful reducing agents easily oxidized by the air to phosphites and then to phosphates, particularly in acid solution. They will reduce concentrated sulphuric acid to sulphur, phosphorus pentachloride to phosphorus, and solutions of copper sulphate to copper, or possibly copper hydride. The acid is decomposed by heat into phosphoric acid and phosphine:

$$2H_3PO_2 = H_3PO_4 + PH_3 \uparrow,$$

but if hypophosphites are boiled in strongly alkaline solution hydrogen is evolved:

$$H_2PO_2' + OH' = HPO_3'' + H_2 \uparrow.$$
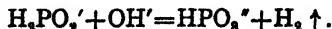
The hypophosphites of the metals are usually obtained from solutions of sulphates and of barium hypophosphite; on heating they generally lose hydrogen and phosphine, and leave a residue of phosphate.

Phosphorous acid, H_3PO_3, and the phosphites.—Phosphorous acid can be obtained by dissolving phosphorus trioxide in water, but this method is very tedious; the hydrolysis of phosphorus trichloride is more convenient. The trichloride is maintained at 60° while a brisk current of air is passed through it, and the vapours are passed into ice-water, which after some time becomes filled with a mass of crystals: these can be filtered, washed, and dried in a vacuum:

$$PCl_3 + 3H_2O = P(OH)_3 + 3HCl.$$
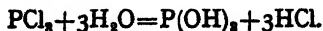
If liquid phosphorus trichloride is added to water the reaction is very violent, and decomposition occurs, but this can be avoided in an alternative method of preparation by the use of concentrated hydrochloric acid instead of water.

Phosphorous acid is a colourless crystalline substance that melts at 74°. The crystals are deliquescent and readily soluble in water. The solutions behave as though they contained a dibasic acid, and the formula of the acid is supposed to be
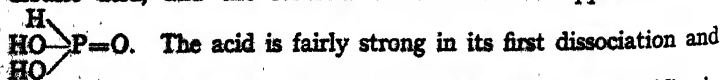
$$\begin{matrix} H \\ HO \\ HO \end{matrix} P = O.$$ The acid is fairly strong in its first dissociation and weak in its second dissociation (compare phosphoric acid); in concentrated solutions associated molecules $(H_3PO_3)_2$ and ions $H_3P_2O_6'$ also make their appearance. As is also the case with phosphoric acid, phosphorous acid can be titrated against

one equivalent of alkali with methyl orange, and two with thymolphthalein.

Phosphorous acid and the phosphites are less powerful reducing agents than the hypophosphites, and are oxidized by atmospheric air, even in acid solution, only in the presence of certain catalysts such as iodine; the product is phosphoric acid. The boiling alkaline solutions do not yield hydrogen so readily as the hypophosphites, but solid phosphorous acid, like hypophosphorous acid, is on heating decomposed into phosphoric acid and phosphine:

$$4H_3PO_3 = 3H_3PO_4 + PH_3 \uparrow .$$

Phosphites will reduce copper sulphate solutions to copper and phosphorus pentachloride to phosphorus, but with concentrated sulphuric acid only sulphur dioxide, and no sulphur, is obtained.

The phosphites are usually prepared by the action of phosphorous acid on bases or carbonates. Both monohydrogen and dihydrogen phosphites are known, but, as already explained, the third hydrogen atom of the molecule cannot be replaced by metals. On heating, the phosphites yield a phosphate together with hydrogen or phosphine, or both. Calcium phosphite, $CaHPO_3.2H_2O$, and barium phosphite, $BaHPO_3$, are only slightly soluble in water, so that phosphite solutions yield precipitates with calcium or barium solutions, a reaction which distinguishes them from the hypophosphites.

Metaphosphorous acid, HPO_2, is obtained as a crystalline solid by the action of dry oxygen on dry phosphine:

$$PH_3 + O_2 = HPO_2 + H_2.$$
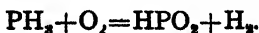
This substance reacts with water to form ordinary or ortho-phosphorous acid:

$$HPO_2 + H_2O = H_3PO_3,$$

and no salts of it have been prepared. Salts have, however, been prepared derived from the very unstable *pyrophosphorous acid*, $H_4P_2O_5(2H_3PO_3 - H_2O)$. They are of small importance.

Hypophosphoric acid, $H_4P_2O_6$, was discovered in 1877 and is usually prepared by the oxidation of red phosphorus by alkali hypochlorite. When phosphorus is allowed to oxidize slowly in the presence of water, about 6 per cent of it is converted into this acid and the remainder to phosphoric acid. Hypophosphoric acid can also be prepared by the oxidation of phosphorus with a hot acid solution of copper nitrate. It can be separated from the other acids of phosphorus also produced in these reactions by precipitation with sodium acetate of the slightly soluble sodium hypophosphate, $Na_2H_2P_2O_6.6H_2O$, which can then be recrystallized from boiling water. From the hot solution lead hypophosphate can be

precipitated," and from a suspension of this salt a solution of the acid can be obtained by treatment with hydrogen sulphide, which precipitates lead sulphide. Concentration of the solution under reduced pressure yields either the anhydrous acid or a hydrate.

Hypophosphoric acid is a colourless crystalline hygroscopic solid melting at 55° and soluble in water. On heating to about 70° it is converted into an equimolecular mixture of phosphorous and metaphosphoric acids:

$$H_4P_2O_6 = H_3PO_3 + HPO_3.$$

The change is irreversible, and takes place equally readily in solution, rapidly on heating but only slowly in the cold, while these acids show no sign of combination on mixing, and none is discernible in the freezing-points of their mixtures. Solutions of hypophosphoric acid or its salts have practically no reducing action, and are unaffected by hydrogen peroxide, dilute nitric acid, or the halogens. On warming they display reducing properties due to the phosphorous acid formed by decomposition.

The acid is tetrabasic, and salts have been prepared in which a quarter, a half, three-quarters, and all the hydrogen has been replaced by a metal. When the acid is titrated against a base with methyl orange, an end-point is reached at a half-way stage, so the acid must be tolerably strong in its first two dissociations. The formula is a matter of controversy, but the suggestion

PO(OH)$_2$
| appears to fit the facts better than any other.
PO(OH)$_2$

Phosphorus tetroxide cannot be regarded as the anhydride of this acid, since neither substance can be directly converted into the other.

PHOSPHORIC ACID exists in three modifications: the ortho-acid, H_3PO_4, the pyro-acid, $H_4P_2O_7$, and the meta-acid, HPO_3, connected as follows with the pentoxide:

$$P_2O_5 + 3H_2O = 2H_3PO_4. \qquad P_2O_5 + 2H_2O = H_4P_2O_7.$$
$$P_2O_5 + H_2O = 2HPO_3.$$
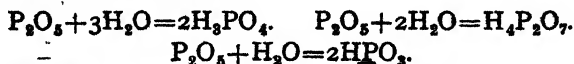
Orthophosphoric acid, H_3PO_4, the most important acid of phosphorus, is obtained by the action of hot water on phosphorus pentoxide, or more readily by oxidizing phosphorus in contact with water, usually with concentrated nitric acid. Dilute acid has little action on phosphorus, but if the acid is too concentrated dangerous explosions may take place. Any variety of phosphorus may be used. In the LILJENROTH process (p. 616) orthophosphoric obtained from phosphorus and steam.

The product of the action of nitric acid or other volatile oxidizing agent on phosphorus and water is evaporated until nearly all the water has been expelled: the mass is then cooled and crystals with the composition H_3PO_4 separate. As hot concentrated phosphoric acid attacks glass, porcelain, and even some varieties of fused silica, this operation must be carried out in a platinum vessel. The product is a colourless crystalline solid melting at 42°, hygroscopic, and very soluble in water. On strong heating it loses water and is converted first to pyrophosphoric and then to metaphosphoric acid.

Orthophosphoric acid is tribasic. The dissociation-constants are $0 \cdot 011$, 2×10^{-7}, and $3 \cdot 6 \times 10^{-13}$, so that it is fairly strong in its first dissociation, weak in its second, and exceedingly weak in its third. Consequently solutions of the dihydrogen phosphates, such as NaH_2PO_4, have an acid reaction, the monohydrogen phosphates, such as Na_2HPO_4, are alkaline from hydrolysis, and the normal phosphates, such as Na_3PO_4, are nearly as alkaline in solution as caustic soda. If the hydrogen ion concentrations of the solutions obtained by adding (say) $M/10$ solutions of caustic alkali to $M/10$ solutions of phosphoric acid are calculated, they are found to be (18°): NaH_2PO_4, $10^{-4.5}$; Na_2HPO_4, $10^{-9.3}$; Na_3PO_4, 10^{-12}, and these values have been confirmed by potentiometric titration. Consequently the acid can be titrated to a dihydrogen phosphate with methyl red and to a monohydrogen phosphate with thymolphthalein, or less accurately with phenolphthalein, while the titration to the normal salt cannot be carried out with indicators; in this region the hydrogen ion concentration changes only slowly with the addition of alkali. Mixtures of phosphoric acid and phosphates are much used as buffers and in the preparation of solutions of standard hydrogen ion concentration.

Orthophosphoric acid in the pure state or in solution is a stable substance with the ordinary properties of an acid but otherwise not reactive. The phosphate ion shares the stability of the neighbouring silicates and sulphates, though the tervalent ion PO_4''' uncombined with hydrogen ions exists only in very concentrated alkaline solution. As the acid is not volatile on moderate heating it can be used instead of sulphuric acid for expelling volatile acids from their salts, but all the phosphates are decomposed by hot concentrated sulphuric acid.

Orthophosphates.—These salts are prepared by the usual methods. All the phosphates and hydrogen phosphates of the alkali-metals (except lithium) and ammonium are soluble in water, but most other phosphates are insoluble or only slightly soluble. The insoluble phosphates or double ammonium phosphates of certain metals, among them magnesium and zinc, are used in their gravimetric analysis. The monohydrogen phosphates on ignition yield

water and pyrophosphates, and the dihydrogen phosphates yield water and metaphosphates. Several orthophosphates are described under the metals.

Pyrophosphoric acid, $H_4P_2O_7$.—Attempts to prepare this acid by the action of water on phosphorus pentoxide have been unsuccessful, but it can be prepared without difficulty by heating the ortho-acid to 250°, or from a mixture of the ortho- and meta-acids:

$$H_3PO_4 + HPO_3 = H_4P_2O_7.$$

In the pure state it is obtained from its sodium salt, which remains when disodium monohydrogen phosphate is heated:

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O \uparrow.$$

This is dissolved in water and precipitated as the insoluble lead salt, which is then suspended in water and treated with hydrogen sulphide. The evaporation of the resulting solution must be carried out under reduced pressure, for on heating the pyro-acid takes up water and forms the ortho-acid.

Pyrophosphoric acid is a syrupy liquid of uncertain melting-point, since undercooling takes place very readily. It is freely soluble in water and is a tetrabasic acid, the dissociation-constants being about 0·14, 0·011, 4×10^{-7} and 10^{-8} in that order. The solutions are stable only at low temperatures and readily form orthophosphates on heating, especially if the solutions are acid.

Pyrophosphates.—These salts are prepared by the usual methods or by heating monohydrogen orthophosphates: the normal salts and the dihydrogen salts are the commonest, and indeed it is doubtful whether the others exist at all. The dihydrogen salts yield metaphosphates and water when heated:

$$Na_2H_2P_2O_7 = 2NaPO_3 + H_2O \uparrow.$$

Metaphosphoric acid, $(HPO_3)_n$, 'glacial phosphoric acid,' is obtained by strongly heating the ortho- or pyro-acids in a gold or platinum vessel, but if the process is carried too far the product contains an excess of phosphorus pentoxide. It is a colourless, glassy, and very deliquescent substance, freely soluble in water, with which it evolves much heat. The solutions gradually change to orthophosphoric acid. In the laboratory metaphosphoric acid is used as a lubricant for taps in apparatus where it will be exposed to substances that attack other lubricants. An acid of monomeric formula HPO_3 does not exist, nor have any corresponding salts been obtained. An anion of *empirical* formula PO_3' arises from the condensation of PO_4''' tetrahedra resulting from a mutual sharing of *two* oxygen atoms in each tetrahedron (cf. phosphorus pentoxide, where *three* oxygens are shared). Thus three tetrahedra can condense in a ring to give trimetaphosphate, $(PO_3)_3'''$ (p. 631):
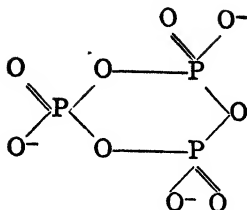
or four to give tetrametaphosphate, $(PO_3)_4''''$; a more widespread condensation yields macromolecular anions of very large molecular weight. The extent of the condensation is controlled mainly by the temperature at which the necessary dehydration of orthophosphate is effected. Fusion of sodium phosphate, NaH_2PO_4, at 600° gives a macromolecular polymetaphosphate, 'sodium phosphate glass,' formerly termed 'hexametaphosphate,' while careful heating at 300° gives the cyclic trimetaphosphate, $Na_3P_3O_9$. Tetrametaphosphoric acid is prepared by treating α-phosphorus pentoxide with ice-cold water.

Analytical distinctions.—When heated with excess of nitric acid and ammonium molybdate, all oxyacids of phosphorus or their salts yield a canary-yellow precipitate of ammonium phosphomolybdate (p. 714). Solutions of the salts of the phosphoric acids can be distinguished as follows:

(i) The insoluble silver salt of orthophosphoric acid is *yellow*, of the other acids *white*.

(ii) Metaphosphoric acid will coagulate a solution of albumen, the other acids will not.

Permonophosphoric acid, H_3PO_5, is obtained in solution by adding phosphorus pentoxide to concentrated ice-cold hydrogen peroxide:

$$P_2O_5 + 2H_2O_2 + H_2O = 2H_3PO_5.$$
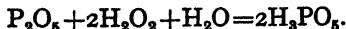
The solutions have powerful oxidizing properties resembling those of permonosulphuric acid. A perdiphosphoric acid, $H_4P_2O_8$, has also been reported.

Comparison of the oxyacids of phosphorus.—A few of the properties of these somewhat confusing substances are shown in the table (p. 632). They are all colourless hygroscopic solids soluble in water, except pyrophosphorous acid and the perphosphoric acids, which are known only in solution.

HALIDES OF PHOSPHORUS.—The principal halides of phosphorus are:

Fluorides	*Chlorides*	*Bromides*	*Iodides*
PF_3, PF_5	PCl_3, PCl_5	PBr_3, PBr_5	P_2I_4, PI_3

and a number of mixed halides are known.

x

Name	Formula	Melting-point	Basicity	Dissociation-constants				Reducing or Oxidizing Properties	Action of Heat
				1	2	3	4		
Hypophosphorous	H_3PO_2	26·5°	1	·01				strong reducing	H_3PO_4 & PH_3
Phosphorous, Ortho- Pyro- Meta-	H_3PO_3 $H_4P_2O_5$ HPO_2	74°	2 2	·02	7×10^{-7}			reducing	H_3PO_4 & PH_3
Hypophosphoric	$H_4P_2O_6$	55°	4	resembles pyrophosphoric				very weak reducing	HPO_3 & H_3PO_3
Phosphoric, Ortho- Pyro- Meta-	H_3PO_4 $H_4P_2O_7$ $(HPO_3)_n$	42° glassy	3 4	·011 ·14 strong	2×10^{-7} ·011	4×10^{-13} 4×10^{-7}	10^{-8}	neither reducing nor oxidizing	$H_4P_2O_7$ $(HPO_3)_n$ volatilizes, some P_2O_5
Permonophosphoric	H_3PO_5							strong oxidizing	
Perdiphosphoric	$H_4P_2O_8$								H_3PO_4, O_2, O_3

COMPARISON OF SOME OF THE KNOWN PROPERTIES OF THE OXYACIDS OF PHOSPHORUS

They are volatile substances usually prepared by the union of the elements. The iodides and higher bromide are yellow, red, or orange; the fluorides, chlorides, and tribromide colourless. They are all decomposed by water with the formation of hydrogen halide, together with phosphorous acid from the trihalides and phosphoric acid from the pentahalides:

$$PF_3+3H_2O=P(OH)_3+3HF. \quad PBr_5+4H_2O=H_3PO_4+5HBr,$$
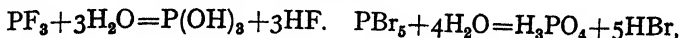
consequently they fume in moist air. The trihalides combine with oxygen on heating, or sometimes in the cold, to form oxyhalides:

$$2PCl_3+O_2=2POCl_3,$$
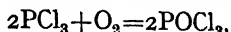
but the tri-iodide does not show this reaction: the pentahalides are stable against oxygen unless strongly heated, when they dissociate in any case into the trihalide and free halogen, the reaction:

$$PX_3+X_2 \rightleftharpoons PX_5$$
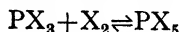
(X represents a halogen atom) being in all cases reversible.

The melting- and boiling-points of the halides are shown in the table:

	PF_3	PCl_3	PBr_3	PI_3	PF_5	PCl_5	P_2I_4
Melting-point	$-152°$	$-94°$	$-42°$	$61°$	$-83°$	circ. $160°$	$110°$
Boiling-point	$-101°$	$75°$	$175°$	decomposes	$-75°$	circ. $160°$	decomposes

MELTING- AND BOILING-POINTS OF THE HALIDES OF PHOSPHORUS

Phosphorus fluorides.—Both the tri- and pentafluorides can be obtained by union of the elements, but the *trifluoride* is best prepared by the interaction of arsenic trifluoride (p. 643) and phosphorus trichloride. It is a colourless gas which unites explosively with oxygen on sparking the mixed gases in the cold:

$$2PF_3+O_2=2POF_3,$$
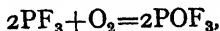
and will combine with fluorine or any of the halogens to form pentahalides. It is hydrolysed by water (contrast nitrogen trifluoride).

The *pentafluoride* was first prepared in 1887 by the action of arsenic trifluoride on phosphorus pentachloride:

$$5AsF_3+3PCl_5=3PF_5\uparrow+5AsCl_3.$$
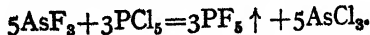
It is a strong-smelling colourless gas which is hydrolysed by water, but in the absence of water it does not attack glass.

Phosphorus trichloride, PCl_3, is commonly prepared by direct

combination in an apparatus similar to that illustrated, in which a brisk current of dry chlorine is passed over the surface of molten phosphorus (the fusion is most safely accomplished with warm water). A flame appears in the retort in which this operation is carried out, and which must be filled with carbon dioxide before the chlorine is admitted, and the heat of the reaction is sufficient to boil the trichloride, which can be purified by a single redistillation. It is a colourless liquid of density 1·6, decomposed by water and
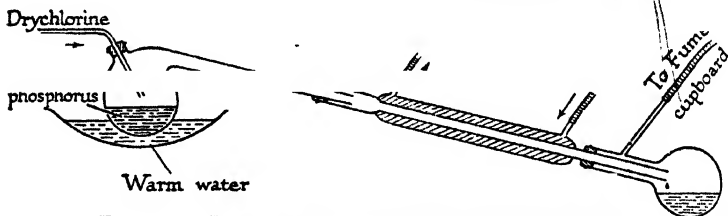
FIG. 131.   PREPARATION OF PHOSPHORUS TRICHLORIDE

other hydroxylic solvents, but soluble in inert organic liquids: it is covalent.

It is a very reactive substance whose chemistry is controlled by (1) the avidity of phosphorus for oxygen or hydroxyl, and (2) its donor properties, which may be attributed to the lone pair of electrons. With water, alcohols, and other organic substances containing hydroxyl groups it forms compounds in which the hydroxyl group is replaced by chlorine, and is sometimes used for this purpose in organic chemistry, though it has largely been superseded by thionyl chloride. It reacts with oxygen on heating, forming the oxychloride $POCl_3$, and is explosively oxidized by nitric acid. With ammonia it forms a compound, $PCl_3.6NH_3$.

Phosphorus pentachloride, PCl_5, is prepared by the action of excess of chlorine on phosphorus trichloride or on phosphorus. As the product so readily reacts with the moisture of the atmosphere it is best to prepare it in the vessel in which it is to be preserved. A quantity of the trichloride (which may be replaced by a concentrated solution of phosphorus in carbon disulphide) is placed in a bottle and a brisk stream of chlorine, which must be dry, is led in through a wide tube. It is best to provide a glass stirrer for use in the later stages of the reaction, during which the bottle must be cooled. When all the trichloride has been converted to the colourless solid pentachloride, the chlorine is driven from the apparatus by a current of dry carbon dioxide and the bottle secured with a well-vaselined stopper.

The colour and vapour-density of phosphorus pentachloride both

indicate partial and fully reversible dissociation into the trichloride and chlorine on heating:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

At 200° about half the pentachloride is dissociated.

The constitution of this compound—i.e. its electronic structure—has been the subject of some speculation. The pentachloride is a covalent compound which in the pure state will not conduct electricity, but the solutions in certain solvents such as nitrobenzene do have this power. X-ray diffraction applied to the crystalline solid has given the explanation, by showing that the pentachloride is formed from equal numbers of the ions $(PCl_6)'$ and $(PCl_4)^{.}$, which when released in solution confer conductivity. The vapour, on the other hand, consists of single molecules, PCl_5, of bipyramidal shape, in the constitution of which the thermal dissociation is not reflected.

FIG. 132. PREPARATION OF PHOSPHORUS PENTACHLORIDE

Phosphorus pentachloride is a powerful chlorinating agent, and is widely used in organic chemistry for this purpose; thus with alcohol:

$$C_2H_5OH + PCl_5 = C_2H_5Cl + HCl \uparrow + POCl_3 \uparrow .$$
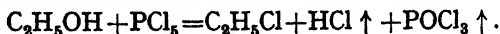
The evolution of hydrogen chloride in the cold is considered to be evidence for the existence of a hydroxyl group in the molecule, but on heating phosphorus pentachloride will chlorinate many compounds which contain no hydroxyl, e.g. ethers.

$$(C_2H_5)_2O + PCl_5 = 2C_2H_5Cl + POCl_3 \uparrow .$$
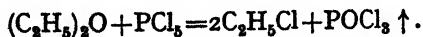
The hydrolysis of the pentachloride yields phosphoric acid and hydrochloric acid, but in the absence of a large excess of water considerable quantities of phosphoryl chloride, $POCl_3$, may be produced. The pentachloride forms two compounds with ammonia: $PCl_5.8NH_3$ and $PCl_5.10NH_3$.

Bromides of phosphorus comprise the tribromide and the pentabromide, both of which are produced by direct union of the elements. The pentabromide melts below 100° to a liquid mixture of the tribromide and bromine containing only a small residue of the pentabromide in equilibrium.

Iodides.—The stablest iodide has the formula P_2I_4, and is prepared by mixing carbon disulphide solutions of the elements in the correct proportions. The tri-iodide PI_3 is much more soluble in carbon disulphide, and this method of preparation is unsuitable: it is made by the action of hydrogen iodide on phosphorus trichloride:

$$PCl_3 + 3HI = PI_3 + 3HCl.$$
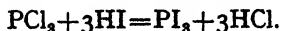
The hydrolysis of the iodides of phosphorus is made use of as a source of hydrogen iodide.

PHOSPHORUS OXYHALIDES.—In addition to the phosphoryl trihalides, POF_3, $POCl_3$, and $POBr_3$, other oxyhalides of less importance are known. The phosphoryl trihalides are produced by oxidation of the trihalides of phosphorus either by heating in the air or otherwise, or by an intermediate stage of the hydrolysis of the phosphorus pentahalides:

$$PCl_5 + H_2O = POCl_3 + HCl.$$
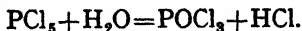
Phosphoryl fluoride is a colourless gas, the chloride is a colourless liquid, and the bromide an orange solid: the melting- and boiling-points are:

	POF_3	$POCl_3$	$POBr_3$
Melting-point	$-68°$	$+2°$	$56°$
Boiling-point	$-40°$	$105°$	$190°$

MELTING- AND BOILING-POINTS OF THE PHOSPHORYL TRIHALIDES

The phosphoryl halides are all hydrolysed by water, the products being phosphoric acid and the hydrogen halide: they fume in the air.

Phosphoryl trichloride, $POCl_3$, usually called simply phosphoryl chloride, is prepared by oxidizing phosphorus trichloride with potassium chlorate. The reaction is violent, and the vessel in which it is carried out must be well cooled and provided with a reflux condenser. The product is finally distilled off. It is used in organic chemistry as a chlorinating agent.

PHOSPHORUS SULPHIDES.—Phosphorus and sulphur react vigorously when heated together, forming a product which contains several of the large number of binary compounds of these elements which have been reported. They may be prepared in the laboratory by mixing finely-powdered red phosphorus with the theoretical quantity of sulphur, and heating the mixture in a current of an inert gas (carbon dioxide) until reaction takes place. The molten mass is then allowed to cool, broken up, and purified by various methods.

Tetraphosphorus trisulphide, P_4S_3, is the most important sulphide of phosphorus, and is the principal ingredient of the mixture used for tipping one kind of match. It is made on the commercial

scale by heating a mixture of sulphur and phosphorus in carbon dioxide to about 330°. When prepared in the laboratory it may be purified by extracting it with carbon disulphide, evaporating to dryness, and boiling it with water, by which it is only very slowly hydrolysed, whereas hot water soon decomposes the other sulphides of phosphorus, forming hydrogen sulphide, phosphoric acid, and other products. It is a yellow crystalline substance melting at 174°; stable in the air, though readily taking fire when heated. In the absence of air and water it can be heated to a high temperature without decomposition.

Tetraphosphorus heptasulphide, P_4S_7, differs from the compound just mentioned by being nearly insoluble in carbon disulphide. It is decomposed by water more rapidly than the pentasulphide.

Phosphorus pentasulphide, P_4S_{10}, is a pale yellow solid, melting-point 290°. Cold water gradually hydrolyses it to ortho-phosphoric acid and hydrogen sulphide.

Phosphorus nitride, $(P_3N_5)_n$.—This interesting compound can be made by a variety of methods, of which the simplest is perhaps that due to STOCK: phosphorus pentasulphide is strongly heated in ammonia. The product is a colourless solid without taste or smell, which must be heated to a high temperature *in vacuo* before it decomposes into its elements. It is unaffected by cold water, but by boiling water is slowly decomposed into phosphoric acid and ammonium phosphate. It burns if strongly heated in the air. On careful heating *in vacuo* at 750° nitrogen is lost, and the nitride of simpler empirical composition PN sublimes as a red solid. The structures of the sulphides have been revealed by X-ray diffraction, but those of the nitrides of phosphorus still await elucidation.

ARSENIC

As $=74.91$. *Atomic Number*, 33

History.—Yellow arsenic sulphide was employed as a pigment by the ancient Assyrians, whence the name *sandarach*, from *šindu arqu*, yellow paint. Both realgar and orpiment (As_4S_4 and As_4S_6) were employed by the Alexandrian and later alchemists, and JABIR knew how to extract the element from them. AL-IRAQI (about 1260) pointed out the resemblance between orpiment and stibnite (Sb_2S_3), while the formation of white arsenic (As_2O_3) has been known at least since the time of PLINY. BRANDT (1774) recognized that white arsenic was the calx of metallic arsenic.

Occurrence and Extraction.—Though not very abundant, arsenic is widely diffused in small quantities. Sulphides are frequently contaminated with arsenides, and the removal of this arsenic is

usually necessary if the sulphides are to be used for the extraction of metals or for the manufacture of sulphur dioxide: the oxides of arsenic are notorious as catalytic poisons, and have caused much difficulty in plants such as those used for the contact process.

The two principal ores of arsenic are the sulphides *realgar*, As_4S_4, and *orpiment*, As_4S_6, but these are not generally worked for the element, which is manufactured by heating certain mixed arsenides, of which *mispickel*, FeSAs, is the most important, in the absence of air. The operation is carried out in retorts not unlike those used for the distillation of zinc (p. 502), and the arsenic, or some of it, sublimes and is collected in sheet-iron condensers. It can be freed from all impurities except antimony by mixing it with charcoal and subliming it. In the laboratory the purest arsenic can be prepared by precipitating arsenious oxide from a solution of a pure arsenite, mixing it with charcoal and distilling the arsenic from the mixture.

Properties.—Arsenic exists in three allotropic modifications, as follows:

1. *Metallic arsenic*, the stablest form, obtained by heating any other form or by slow sublimation. It is a brittle grey substance of density 5·7, a conductor of electricity, and sublimes on strong heating, the vapour pressure reaching 760 mm. at about 620°.

2. *Yellow arsenic* is obtained when arsenic vapour is suddenly cooled, and is metastable at ordinary temperatures. It is very much less dense than the other forms of arsenic (density 2·1), and is the only modification to be soluble in carbon disulphide. In the solid state it rapidly changes into the grey form, particularly when exposed to light, and if it is to be preserved it must therefore be dissolved in carbon disulphide as soon as it is produced. It is a translucent substance which does not conduct electricity. The boiling-point of the solutions indicates a molecule As_4.

3. *Black arsenic* is slowly precipitated from carbon disulphide solutions of the yellow variety, and is also the first product of the transformation of the solid form of this substance in the cold. It differs from metallic arsenic in its smaller density (4·6), by being translucent, in its greater resistance to oxidation by air or nitric acid, and by not possessing the power of conducting electricity.

Amorphous arsenic is obtained as a brown powder by reducing arsenic compounds with such substances as stannous chloride or sodium hydrosulphite. It is an amorphous substance of variable density—4·0 is a representative value.

At atmospheric pressure and near the sublimation temperature the vapour of arsenic consists chiefly of tetra-atomic molecules, but if the pressure is reduced or the temperature increased, the mean molecular weight diminishes and single atoms make their appearance.

Like phosphorus, arsenic can be made to exhibit phosphorescence when heated in air or oxygen, but the phenomenon is less conspicuous and a temperature of 200° is necessary. If heated in air or oxygen, arsenic burns to form the trioxide As_2O_3.

The standard electrode potential of metallic arsenic is about $+0.3$ volt, so it will not dissolve to any considerable extent in acid solutions, unless these have an oxidizing action. By boiling concentrated sulphuric acid, or by nitric acid, it is converted to the trioxide or to arsenic acid. It will not combine with hydrogen, unless nascent, but it combines energetically with the halogens. Arsenic will deposit the metal from solutions of salts of silver, copper, gold, or mercury.

Arsenic hydride, arsine, AsH_3.—This is the only known hydride of arsenic, though organic derivatives of the hypothetical hydrides As_2H_2 and As_2H_4 are well known. It is obtained by the action of nascent hydrogen on arsenic, which may be present as the element or in solution as arsenious acid. The product of this reaction contains a large proportion of hydrogen, and the pure gas must be obtained by the action of acids on arsenides; the arsenides of sodium and calcium have been recommended.

$$Na_3As + 3H^{\cdot} = AsH_3 \uparrow + 3Na^{\cdot}.$$
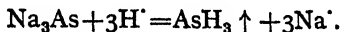
The product of this reaction also contains hydrogen. It is first dried and then condensed in a freezing-mixture at about $-90°$, which allows the hydrogen to pass on.

Arsine is a colourless gas with a repulsive smell resembling that of garlic. It is intensely poisonous even in great dilution, and has caused the death of more than one investigator. It can be condensed to a liquid at $-55°$; this liquid freezes at $-113°$. The gas is scarcely soluble in water and is little affected by acids or alkalis, but it dissolves freely in turpentine. It is unstable, and when heated to 200° or so, or exposed to sunlight, decomposes into its elements. The decomposition is accelerated by various catalysts: even pure arsine slowly decomposes in the dark or in the light. The decomposition of arsine by heat is the basis of the celebrated Marsh test for arsenic (p. 646). It is readily converted to water and arsenious or arsenic acid by oxidizing agents, and can be absorbed by a solution of silver nitrate, from which it precipitates silver:

$$AsH_3 + 6Ag^{\cdot} + 3H_2O = AsO_3''' + 6Ag \downarrow + 9H^{\cdot}.$$
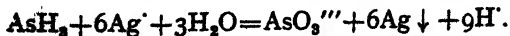
Arsenides.—A large number of these compounds occur native in an impure form, e.g. Ag_3As, $CoAs_2$. In the laboratory they are usually prepared by direct combination, either by heating the element with arsenic or by passing the vapour of arsenic over the

*X

element, but occasionally arsenates are reduced; thus calcium arsenide, Ca_3As_2, is prepared by heating calcium arsenate with coke in the electric furnace (compare calcium phosphide). The arsenides are usually dark-coloured solids, sometimes transparent. The arsenides of the alkali-metals, alkaline-earth metals, and aluminium are sufficiently soluble to be decomposed by water into arsine and hydroxides, the other arsenides are mostly insoluble in water, but are oxidized to arsenates by hot nitric acid.

OXIDES OF ARSENIC.—The principal oxides of arsenic are the sesquioxide or trioxide, As_2O_3, and the pentoxide, As_2O_5: a tetroxide, As_2O_4, is also known. The formulae given are empirical.

Arsenic trioxide, arsenious oxide, As_2O_3, is formed when arsenic burns in air or oxygen, but the arsenious oxide of commerce is a by-product of the extraction of certain metals, notably tin, from their arsenic-containing ores. The vapours from the roasted ore contain sulphur dioxide and arsenious oxide, and the latter is caused to settle in a dust-collecting plant and purified by sublimation. Pure arsenious oxide can be precipitated from a solution of pure sodium arsenate by sulphur dioxide:

$$2AsO_4''' + 2SO_2 + H_2O = As_2O_3 \downarrow + 2SO_4'' + 2OH'.$$
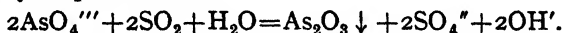
The oxide exists not only in the crystalline form, but as an under-cooled liquid called vitreous arsenic trioxide, obtained by condensing the vapour on a relatively hot surface. Both forms are colourless. The vitreous form slowly reverts to the crystalline form on keeping, though by the exclusion of air the transformation can be almost indefinitely retarded. The crystalline oxide sublimes on heating, but the vitreous oxide melts and then boils. The vapour density at fairly low temperatures corresponds with the formula As_4O_6, but at higher temperatures molecules of As_2O_3 are found in the vapour; the crystal unit, as determined by the X-ray method, also corresponds with a molecule As_4O_6.

Arsenious oxide is slightly soluble in water, and the unstable or vitreous form has a markedly higher solubility than the crystalline form. At room temperature the solubilities are about 37 and 17 gm. per litre respectively, and the solubility increases with the temperature. The oxide is amphoteric, and is more soluble in acids or in bases than in water. The aqueous solution has weakly acid properties, and is said to contain arsenious acid, H_3AsO_3. It is monobasic, and the dissociation-constant is of the order 10^{-8}–10^{-10}, so the acid is very weak.

Arsenious oxide can be reduced to arsenic by heating in hydrogen or carbon monoxide, but arsenious acid and the arsenites are fairly powerful reducing agents, being converted to arsenates:

$$AsO_3''' + O \rightarrow AsO_4'''.$$
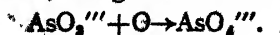
Arsenites.—The complexity of these compounds recalls that of the oxyacids and salts of phosphorus. The arsenites of the alkali-metals and ammonium are obtained by dissolving the oxide in the base and are soluble in water; they are used in volumetric analysis as reducing agents, particularly for the titration of iodine, but the solution must be buffered:

$$AsO_3''' + I_2 + H_2O = AsO_4''' + 2I' + 2H\dot{}.$$
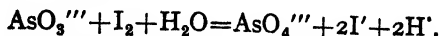
Periodates or iodates can also be reduced to iodides. With neutral solutions of silver nitrate a precipitate of yellow silver orthoarsenite, Ag_3AsO_3, is obtained, but if sufficient ammonia is present the silver nitrate is reduced to silver:

$$AsO_3''' + 2Ag\dot{} + H_2O = AsO_4''' + 2Ag \downarrow + 2H\dot{}.$$
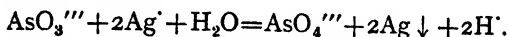
It is obvious that the reduction will be favoured by an alkaline solution.

Sodium arsenite is obtained in solution by dissolving arsenious oxide in caustic soda. If the arsenites of sodium are required pure and anhydrous, they may be prepared as follows:

1. Sodium orthoarsenite, Na_3AsO_3, is insoluble in alcohol, and is obtained by heating arsenious oxide with alcoholic caustic soda and extracting with alcohol.

2. Sodium metarsenite, $NaAsO_2$, is prepared by dissolving arsenious oxide in a hot solution of sodium carbonate until no more action takes place: the solution is then evaporated to dryness. Both these salts are soluble in water. The solutions have an alkaline re-action from hydrolysis, and if acids are added to them arsenious oxide is precipitated; even a solution of carbon dioxide is acid enough for the purpose. When required for reducing purposes the solutions are therefore usually kept alkaline.

Copper arsenite can be obtained as a precipitate of variable composition from a solution of copper sulphate and a solution of arsenious oxide in potassium carbonate. It was formerly used as a green pigment under the name of 'Scheele's green,' but the sale of pigments containing arsenic is now illegal in most countries.

Arsenic tetroxide, As_4O_8, is obtained by heating the trioxide and the pentoxide in equimolecular proportions. No series of salts is derived from it.

Arsenic pentoxide, As_4O_{10}, is obtained by the oxidation of the trioxide. The operation is usually carried out by boiling this substance with concentrated nitric acid. When the action is over the liquid is decanted and the residue freed from water and nitric acid at a low red heat.

The pentoxide is a white powder which, like arsenious oxide, can also exist in the vitreous or undercooled condition. It decomposes

on heating to about 400° into oxygen and arsenious oxide, which volatilizes; this decomposition takes place before it melts. The solid is hygroscopic and dissolves in water to form a solution said to contain arsenic acid, H_3AsO_4, but it has not the exceptional drying properties of the pentoxide of phosphorus. Whether in the dry state or in solution it is an oxidizing agent. It can be reduced to arsenic by means of hydrogen.

The pentoxide dissolves only slowly in cold water, but more rapidly on heating, though the solubility is high at all temperatures, and the saturated solution has a density of more than 2. Arsenic acid is rather weaker than orthophosphoric acid. The first dissociation-constant is about 5×10^{-3}, and the second and third constants lower than the corresponding values for phosphoric acid; the acid can be titrated as a monobasic acid with methyl orange and as a dibasic acid with phenolphthalein. Solutions of the arsenates are therefore considerably hydrolysed.

Arsenates can be reduced to arsine by nascent hydrogen in acid solution:

$$H_3AsO_4 + 8H = AsH_3 \uparrow + 4H_2O,$$
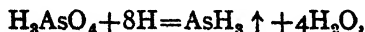
but in alkaline solution this reaction will not take place—this is one of the distinctions between arsenates and arsenites. The oxidizing power of the arsenates is not very great; they will liberate bromine or iodine from acid solutions of bromides or iodides, but with chlorides the reaction is far from complete. As already noted, *sulphur dioxide precipitates arsenious oxide from arsenate solutions.* Hydrogen sulphide precipitates arsenic pentasulphide from acid solutions:

$$2AsO_4''' + 6H^{\cdot} + 5H_2S = As_2S_5 \downarrow + 8H_2O,$$

but if the temperature is raised, arsenic trisulphide and free sulphur also make their appearance.

Arsenates.—These compounds are usually obtained by the interaction of arsenic pentoxide with a base, but they may also be prepared by oxidizing arsenic in the presence of suitable salts, e.g. potassium arsenate can be obtained by heating arsenic with potassium chlorate, or arsenious oxide with potassium nitrate. Orthoarsenates derived from H_3AsO_4, pyroarsenates derived from $H_4As_2O_7$, and metarsenates derived from $HAsO_3$, are all known.

Disodium hydrogen orthoarsenate, $Na_2HAsO_4.7H_2O$, is prepared on the commercial scale by heating a mixture of sodium arsenite and sodium nitrate in a furnace. It can also be made from arsenic acid and sodium carbonate solution. It is a colourless compound used in calico-printing; like all the arsenates of the alkali-metals and ammonium it is soluble in water.

When treated with hot nitric acid solutions of ammonium

molybdate, arsenate solutions all deposit yellow precipitates consisting of complex arsenomolybdates. In this the arsenates resemble the phosphates, but they can readily be distinguished from the phosphates by their oxidizing powers.

ARSENIC HALIDES. — In these compounds the intermediate character of arsenic between the non-metal phosphorus and the metals antimony and bismuth is very clearly marked. Arsenic forms trihalides with all the halogens, a pentafluoride, and a di-iodide, and perhaps a monoiodide. The melting- and boiling-points of the halides are as follows:

	AsF_3	$AsCl_3$	$AsBr_3$	AsI_3	AsF_5	As_2I_4
Melting-point	−8°	−18°	33°	146°	−80°	130°
Boiling-point	64°	130°	220°	(400°)	−53°	380°

THE PRINCIPAL HALIDES OF ARSENIC

They are all decomposed by water, except the tri-iodide, which is fairly stable in solution: as with the corresponding compounds of phosphorus, the first products are oxyhalides and the final products an oxyacid and a hydrogen halide.

Arsenic trifluoride, AsF_3, can be prepared by union of the elements, but the preparation of fluorine can be avoided by distilling a mixture of calcium fluoride and arsenious oxide with concentrated sulphuric acid. It is a colourless volatile liquid with a peculiar smell. As it is fairly easily obtained, it is sometimes used in the preparation of fluorides of other elements, e.g. of phosphorus (p. 633).

Arsenic pentafluoride, AsF_5, is obtained by the continued action of fluorine on the trifluoride. It is a colourless gas which is decomposed by water.

Arsenic trichloride, $AsCl_3$, is the most important of the halides of arsenic, and was once known as 'butter of arsenic.' Arsenic burns when gently heated in chlorine gas (if finely divided it takes fire spontaneously), and the trichloride can be obtained by the action of chlorine on the element or on many of its compounds, such as the trioxide. If the element is used the operation is usually carried out in a retort, and the trichloride purified by distillation. The volatility of the trichloride allows arsenic to be removed in this form from solutions, and this was formerly made use of in one process for the de-arsenification of sulphuric acid, but it is now more usual to remove the arsenic from the reactant gases.

Arsenic trichloride is a colourless fuming liquid of density 2·2. Its vapour has a density corresponding with the formula $AsCl_3$. As the hydrolysis of the trichloride produces arsenious acid the

vapour of this substance is extremely poisonous. The liquid is a non-conductor of electricity, but it forms ionized solutions with such salts as will dissolve in it: in this it resembles hydrogen chloride. The reaction with water:

$$2AsCl_3 + 3H_2O \rightleftharpoons As_2O_3 + 6HCl,$$

is to some extent reversible, since arsenious oxide is much more soluble in concentrated hydrochloric acid than in water: the addition of water to arsenic trichloride may or may not produce a precipitate of the trioxide, according to the temperature and the proportions. The trichloride will dissolve large quantities of chlorine, especially at low temperatures, but it is all given off again on heating, and the hydrolysis of such a solution produces no arsenic acid, only arsenious acid. This and other evidence makes the existence of a pentachloride unlikely.

It is interesting to note that the bromine or iodine in electrovalent bromides or iodides will displace chlorine from arsenic trichloride when bromides or iodides are heated with this compound. The reaction is not always complete, but the most electronegative of the three halogens—i.e. chlorine—most readily enters into electrovalent combination.

Arsenic iodides.—Like phosphorus, arsenic forms both a tri-iodide and a di-iodide, As_2I_4. Each iodide can be obtained by direct union of the elements in suitable conditions, the former in carbon disulphide, the latter in a sealed tube at 230°. The *tri-iodide* is a red solid which is less affected by water than the other halides of arsenic, and can be recovered unchanged from solutions in hydriodic acid. The *di-iodide*, which forms red crystals, is less stable than the tri-iodide, is readily oxidized in the air, and is decomposed by water with the precipitation of arsenic, the first stage of the reaction being:

$$3As_2I_4 = 4AsI_3 + 2As \downarrow.$$

The molecular weight of arsenic di-iodide in carbon disulphide solution is found to correspond with the formula As_2I_4.

ARSENIC SULPHIDES.—Arsenic forms three well-defined sulphides with the formulae As_4S_6, As_4S_{10}, and As_4S_4, and other sulphides have been described.

Arsenic trisulphide, As_4S_6, is found native in many parts of the world, and is known as *orpiment*. It is used as a pigment, and is manufactured for this purpose by sublimation of a mixture of arsenious oxide and sulphur. In the laboratory it can be prepared by precipitating arsenious solutions with hydrogen sulphide. If the solution is acid a yellow precipitate is obtained, but in neutral solution the product is a stable colloidal solution of the trisulphide:

solutions of this substance and of antimony trisulphide are so easily prepared that they have been used for many experiments on colloids.

The trisulphide is easily oxidized by heating in the air, with production of the trioxide, but if heated in the absence of air it melts at about 320° and boils at about 700°. It is not among the least soluble of the sulphides, and is slightly hydrolysed by boiling water, while concentrated acid solutions liberate from it hydrogen sulphide. It is easily oxidized by nitric acid. It dissolves in a solution of ammonium polysulphide, forming a thioarsenite (see below), and this is made use of in analytical chemistry for the separation of arsenic (and antimony) from other elements. It is also soluble in caustic alkalis: the solutions contain compounds in which the oxygen of the arsenites has been partly or wholly replaced by sulphur, and which are therefore called thioarsenites. A large number of such compounds is known, corresponding with the various arsenites, and produced by reactions similar to the following:

$$As_4S_6 + 4OH' = 3AsS_2' + AsO_2' + 2H_2O.$$

Arsenic pentasulphide can be precipitated by hydrogen sulphide from cold very acid solutions of arsenates:

$$2AsO_4''' + 6H^. + 5H_2S = As_2S_5 \downarrow + 8H_2O.$$

If hydrochloric acid is used it must be cautiously mixed with the arsenate solution, for chlorine is evolved if the temperature rises too high.

The pentasulphide resembles the trisulphide in appearance, and when heated to about 500° yields the trisulphide and sulphur. Heated in air at lower temperatures it slowly becomes covered with arsenious oxide, and it is hydrolysed by boiling, but not perceptibly by cold water. It dissolves in alkaline solutions to form thio-arsenates which bear the same relation to the arsenates as do the thioarsenites to the arsenites; they are derived from such acids as H_3AsS_4, $HAsS_2$, and $H_4As_2S_7$.

Arsenic disulphide, As_4S_4, occurs native as *realgar* in many parts of the world, and is used as a red pigment. It can readily be made artificially by distilling a mixture of sulphur with excess of arsenic. The colour of the product, and hence its commercial value, depend on the relative proportions used and on the other details of the preparation.

It is a red or reddish-yellow solid which melts at 310°, boils at 565°, and can easily be sublimed in the absence of air, but if strongly heated in air it burns. The vapour is yellow and can be shown by vapour-density measurements to be composed of As_4S_4 molecules at temperatures not far above the boiling-point. It is insoluble in cold water and decomposed by boiling water.

PHYSIOLOGICAL ACTION OF ARSENIC.—All the soluble compounds of arsenic are virulent poisons, and arsenic in various forms has been used by poisoners for centuries, usually in the form of ' white arsenic,' arsenious oxide.   Immunity can be gained by small doses gradually increased, and in some parts of Europe (e.g. southern Austria) the practice of arsenic-eating is believed to improve the health.   Once acquired, the habit cannot safely be relinquished, and it is said that employees in arsenic works are obliged to take arsenic with them when they go on holiday, as they otherwise suffer in health from the lack of the small quantities that normally enter their system.   Organic compounds of arsenic are administered in small doses in medicine.

Detection and Estimation.—Arsenic is fortunately among the most easily recognized of poisons.   The bodies of those who have died from its administration are often well preserved, a fact that can be attributed to the toxic effect of the arsenic on the bacteria of decomposition.   Arsenic can be separated from organic matter by heating the latter with excess of sodium chloride and a little concentrated sulphuric acid; the arsenic distils over as the volatile arsenic trichloride, which is received in water.   Hydrogen sulphide then precipitates the trisulphide from the solution.   If only small quantities of this substance are obtained they can best be estimated by the well-known test first described by MARSH (1836), and named after him.

In this test the solution suspected to contain arsenic is added to a solution in which hydrogen is being generated.   The arsenic is converted to arsine, AsH_3, and if the issuing hydrogen is heated in a combustion-tube the arsine will be decomposed into its elements and a stain of arsenic will appear on the glass.   The hydrogen was formerly generated from zinc and hydrochloric acid, but an electrolytic method is now almost universal.   However pure the zinc used, it was never possible to prove with absolute certainty that the pieces used in the test really contained no arsenic, even though a number of other pieces from the same sample contained none. In the electrolytic method the hydrogen is generated by the electrolysis of dilute sulphuric acid with a mercury cathode.   These substances are both liquids, and if the apparatus gives a blank result before the suspected solution is introduced it cannot be suggested that any arsenic found was originally present in the reagents.

The anode and cathode compartments are separated by a porous diaphragm, and the whole cell is immersed in a cooling bath to prevent the premature decomposition of any arsine.   The hydrogen issuing from the cathode compartment is dried by calcium chloride and then passes into the combustion-tube, a section of which

is electrically heated. A mirror, if any is obtained, will appear at this place. Any antimony present in the solution will form a mirror together with the arsenic, but it can be distinguished
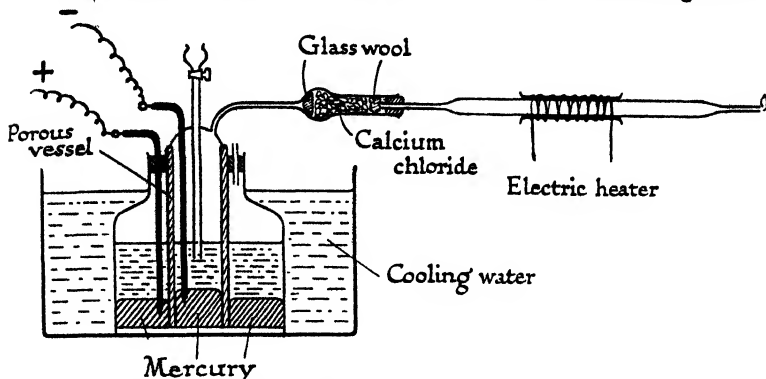
FIG. 133. MARSH TEST FOR ARSENIC (ELECTROLYTIC)

by its insolubility in a hypochlorite solution. The quantity of arsenic present is estimated by comparing the mirror with other mirrors made from known quantities of arsenic.

ANTIMONY

Sb=121·76. *Atomic Number*, 51

History.—JEZEBEL painted her eyes with stibium (Sb_2S_3), but is not to be regarded as an innovator of fashion, since the custom was widespread in ancient Egypt and the civilizations of Mesopotamia. Objects of metallic antimony dating from some thousands of years before Christ have been excavated, and the Moslem alchemists were well acquainted with methods of preparing the element from its sulphide, which they called *kuhl* or *kohol*. The name ' antimony ' is probably derived from the Greek ἀνθεμώνιον, anthemonion, which was given to antimony sulphide on account of the petal-like appearance of the crystals in the naturally-occurring mineral. BASIL VALENTINE, a pseudonymous writer of the early seventeenth century, made a thorough investigation of antimony and many of its compounds, and published his results in the celebrated monograph, *The Triumphal Chariot of Antimony*. ' Butter of antimony ' ($SbCl_3$) was prepared by GLAUBER, who correctly interpreted the reaction between mercuric chloride and antimony sulphide, while *powder of Algaroth* (so named after ALGAROTTO, about 1680, who

used it in medicine) was credited with wonderful qualities of rejuvenating power by PARACELSUS (1493–1541).

Occurrence and Extraction.—Antimony is not a very abundant element. It occurs native, but the deposits are of no importance, and the principal ore, called *stibnite*, is the trisulphide Sb_2S_3. Antimony ores occur in many parts of the world, including North and South America, China, and France.

Unless the ore is an unusually rich one it must be concentrated before the reduction of the sulphide to the metal is attempted. This is usually done by melting the sulphide in perforated pots, through which it drips into vessels placed to receive it, while the infusible impurities are retained. Several methods are available for the reduction of the sulphide. In one method the sulphide is heated with iron:

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$
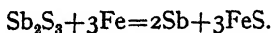
Common salt is added to the mixture to produce a liquid slag with the ferrous sulphide; this slag forms an upper layer which can be removed. In another process the sulphide is raised to a high temperature in a current of air, to which steam may be added, and is thereby converted to the volatile trioxide Sb_2O_3, which is collected in receivers. This trioxide is reduced to the metal by heating with coal, but to prevent its volatilization at the temperature necessary a flux such as sodium sulphate is added which forms a liquid slag under which the metal collects. Electrolytic processes have also been devised.

Uses and Refinement.—Metallic antimony is chiefly used in the manufacture of type-metal and other cast alloys, to which it gives hardness.

Commercial unrefined antimony seldom attains a high degree of purity, and the metal is usually refined by fusing it in crucibles with various substances, such as caustic soda, to remove sulphur, or common salt to remove the more volatile chlorides. In the laboratory the purest antimony is prepared from antimony pentachloride, $SbCl_5$, which is first distilled under reduced pressure, then allowed to react with concentrated hydrochloric acid, with which it forms a compound chloroantimonic acid, a complex of hydrogen chloride, antimony pentachloride, and water. This substance is precipitated in the cold, and by recrystallization from concentrated hydrochloric acid can be obtained very pure. A dilute solution of ammonia converts it by hydrolysis to antimonic acid, which is heated, mixed with potassium cyanide as reducing agent, and melted in a crucible. The resulting mass of antimony is then ready for use.

Allotropic Forms.—This element exists in four distinct

forms, and like other metals can also be prepared in the colloidal state.

Grey or ordinary antimony is a stable crystalline substance with a density of 6·7, and metallic conductivity.

Yellow antimony is much less stable than the corresponding varieties of phosphorus and arsenic, and very low temperatures are required for its preparation. It can be obtained by passing oxygen and antimony hydride into liquid ethane at −100°:

$$4SbH_3 + 3O_2 = 4Sb \downarrow + 6H_2O,$$
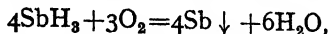
and blackens rapidly even at very low temperatures.

Black antimony.—This form is unstable at room temperature, and can be obtained by rapidly cooling antimony vapour, preferably on a surface cooled with liquid air. It is chemically more reactive than the ordinary variety, and is oxidized at a much lower temperature by the air, and is also less dense (density 5·3). It reverts to the grey variety on heating.

Amorphous or explosive antimony is an impure form obtained on the cathode by the electrolysis of concentrated solutions of antimony trichloride in hydrochloric acid. It is always associated with a small percentage of the chloride. It can be kept indefinitely at room temperature, but if heated to 125° or over, or if sharply struck or even scratched, it grows hot and reverts to the crystalline form, simultaneously emitting fumes of antimony trichloride. It has been shown by the X-ray method to be amorphous. This variety is unstable at all temperatures; its density is 5·8.

General Properties.—Ordinary antimony is a soft grey metal which melts at 630° and boils at 1325°, with electrical conductivity about 4 per cent of that of silver. The vapour density corresponds with Sb_3 at low temperatures and with Sb above 2000°. Its standard electrode potential is probably rather less than that of bismuth, and may be about +0·2 volt; it is in any case not far from that of hydrogen, and antimony will not dissolve in hydrochloric or sulphuric acids, whether concentrated or dilute, in the cold.

Antimony will burn in air or oxygen, forming the trioxide, but it must be strongly heated first. In the presence of water the metal can be oxidized at a lower temperature—e.g. by blowing air through a suspension of the finely-divided metal in boiling water. Antimony reacts very vigorously with the halogens, and less vigorously with phosphorus and sulphur, but it will not combine directly with hydrogen at any temperature. It is a less effective reducing agent than arsenic, and will not, for example, reduce solutions of mercuric salts.

Antimony hydride, stibine, SbH_3.—This is the only known compound of antimony and hydrogen. It can be produced by the

action of nascent hydrogen, either electrolytic or from zinc and acids, on antimony compounds, these methods being very similar to those used for the preparation of arsine, but is more generally prepared by the action of dilute acids on an alloy of antimony and magnesium. This substance, prepared by heating the metals together in a stream of hydrogen, is placed in an apparatus not unlike that used in the preparation of the hydrides of boron (p. 522), and is gradually added to an excess of dilute hydrochloric acid, kept at 0° to minimize the decomposition of the product. The issuing gas consists of stibine with a large excess of hydrogen; it is washed, dried, and passed through a condenser cooled with liquid air, in which the stibine collects. It may be purified by fractional distillation at a low temperature.

Stibine is a colourless gas which can be condensed to a liquid at −17° and to a solid at −88°. It has a peculiar smell and is probably as dangerous a poison as arsine. It is an unstable gas which even at low temperatures readily decomposes into its elements, the change taking place for the most part on the walls of the containing vessel (compare the much stabler phosphine). Consequently it can be kept for a few days at longest. It is decomposed by heat even more easily than arsine, and antimony compounds give a positive result in Marsh's test (p. 646), though the antimony mirror can without difficulty be distinguished from arsenic by its insolubility in hypochlorite solutions, and by other methods. Stibine is not very soluble in water, but it can be absorbed by solutions of silver nitrate, from which it precipitates silver, antimony, and other substances.

Antimonides.—These substances are usually prepared by union of the elements, but a few of them occur native. They resemble the arsenides, but are less stable towards air and water; some of them can be ignited by percussion.

OXIDES OF ANTIMONY.—Antimony forms a trioxide, a tetroxide, and a pentoxide; these compounds having the formulae Sb_4O_6, Sb_2O_4, and Sb_2O_5.

Antimony trioxide, antimonious oxide, Sb_4O_6, is one of the products of combustion of the metal in air or oxygen at comparatively low temperatures, but considerable quantities of other oxides, notably the tetroxide, are produced at the same time; and as this also applies to the roasting of the sulphide, a wet method of preparation is usually preferred. Solutions of antimonious salts may be precipitated with ammonia:

$$2Sb^{\cdots}+6OH'=Sb_4O_6\downarrow+3H_2O,$$

but if caustic alkali is used the precipitate is soluble in excess, forming an antimonite solution.

The trioxide is a colourless solid which melts at 548° and boils at above 1500°; in the absence of air it can be distilled. The vapour density corresponds with the molecule Sb_4O_6, but this dissociates at very high temperatures. When strongly heated in air the trioxide burns with the formation of higher oxides. It is nearly insoluble in water—only 0·1 gm. per litre at 100°—so antimonious acid cannot be directly prepared from it. The trioxide is, however, soluble in either acids or bases, and is amphoteric. Like arsenic trioxide, it can be reduced to the metal by heating in a current of hydrogen, but it is a less vigorous reducing agent. By fusion with sodium or potassium nitrate an antimonate is obtained.

When antimony trioxide is boiled with a solution of potassium hydrogen tartrate, a solution of *potassium antimonyl tartrate*, 'tartar emetic,' $(K(SbO)C_4H_4O_6)_2.H_2O$, is obtained. This is one of the commonest compounds of antimony, and is used in medicine as an emetic, but in quite moderate doses it is a dangerous poison. It is also used as a mordant.

Antimonious acid and the antimonites.—Compounds of antimony trioxide and water have been obtained by indirect methods, and may be classified as 'antimonious acids.' Antimonites may be obtained without difficulty by treating the trioxide with bases either in the solid state or in solution. The considerable hydrolysis of these solutions indicates that antimonious acid, as would be expected from the amphoteric nature of the trioxide, is a very weak electrolyte. The antimonites are less stable and less important than the arsenites.

Sodium antimonite, $NaSbO_2.3H_2O$, is obtained by boiling the trioxide with concentrated caustic soda:

$$Sb_4O_6+4NaOH=4NaSbO_2+2H_2O,$$
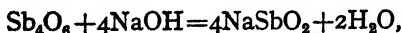
and is one of the few sodium salts to be nearly insoluble in water (see also sodium antimonate); it is, however, hydrolysed by boiling water.

Antimony tetroxide, Sb_2O_4, is the oxide of antimony most stable in air in the region 600°–700°, and is prepared by prolonged ignition of either of the other oxides at this temperature. Overheating leads to loss of oxygen and formation of trioxide. The tetroxide is a colourless solid which decomposes before it melts. It is not markedly soluble in water or in acids, but when fused with alkalis it forms a series of compounds, with formulae such as $K_2Sb_2O_5$ or $K_2Sb_4O_9$, called the *hypoantimonates*. Some of these are soluble in water and yield solutions with oxidizing powers; they will, for example, liberate iodine from acid iodide solutions. This power of forming a series of salts distinguishes the tetroxide of antimony from that of arsenic.

Antimony pentoxide, Sb_2O_5, is precipitated when a solution of an antimonate is acidified, preferably with nitric acid, and can also be prepared by boiling one of the lower oxides with concentrated nitric acid and evaporating once or twice to dryness with fresh acid. The residue must not be heated to too high a temperature or it loses oxygen to form the tetroxide, but it tenaciously retains water, so it must be dried by careful and prolonged ignition at rather less than 400°.

It is a pale yellow substance which darkens on heating and decomposes before it melts. It is only slightly soluble in water, nor does it readily dissolve in acids, but it will dissolve slowly in solutions of the caustic alkalis, forming antimonates. Its small solubility in water distinguishes it from the pentoxide of arsenic.

Antimonic acid and the antimonates.—The formulae of these salts differ from those of the phosphates and arsenates, because antimony readily becomes six-covalent (cf. stannates and plumbates).

Potassium antimonate, $KSb(OH)_6.\frac{1}{2}H_2O$, is prepared by fusing the pentoxide with caustic potash, or by fusing potassium antimonyl tartrate with potassium nitrate and recrystallizing the product from water, in which it is not very soluble.

Sodium antimonate, $NaSb(OH)_6$, is one of the few nearly insoluble salts of sodium, and is sometimes used in analysis. It is precipitated when sodium salt solutions are mixed with solutions of potassium antimonate, and when dried at 100° has the composition shown by the formula.

Antimonic acids of various formulae are precipitated by acidifying solutions of these and other antimonates; they are weak acids only slightly soluble in water. The acids and their salts are feeble oxidizing agents which will liberate iodine from acid iodide solutions.

ANTIMONY HALIDES.—The melting- and boiling-points of the principal halides of antimony are shown in the following table:

	SbF_3	$SbCl_3$	$SbBr_3$	SbI_3	SbF_5	$SbCl_5$
Melting-point	290°	73°	96°	167°	7°	5°
Boiling-point	subl.	221°	288°	(400°)	150°	decomp.

— THE PRINCIPAL HALIDES OF ANTIMONY

They can all be prepared by direct combination, which is always accompanied by the evolution of heat and light. They are very hygroscopic substances, and with the exception of the tri-iodide are colourless. They are all very soluble in water, and are less easily hydrolysed than the halides of arsenic, for it is often possible to recover them by evaporation of their aqueous solutions if these are sufficiently concentrated. By warming in the air they are readily converted to oxides or oxyhalides.

They are more salt-like in character than the halides of arsenic, but have many covalent properties. Thus they are poor conductors of electricity and are soluble in organic solvents, while they are much too volatile to be true salts.

Antimony trifluoride, SbF$_3$, is prepared by dissolving the trioxide in hydrofluoric acid and evaporating until crystals begin to appear. Like all fluorides which are easily hydrolysed, it cannot be kept in glass vessels: gutta-percha or celluloid is usually preferred for this purpose. It is a colourless solid which does not fume in the air, and can be recovered from its solutions (it is exceedingly soluble in water) by evaporation, but it is slowly hydrolysed by moist air.

It readily forms complexes with many classes of substances, including gaseous ammonia and the fluorides of the metals; thus with potassium fluoride it forms a compound, KSbF$_4$, very soluble in water, and yielding in solution the ion SbF$_4$'.

Antimony pentafluoride, SbF$_5$, prepared by union of the elements, is a colourless and very hygroscopic liquid. It is very soluble in water, which does not immediately hydrolyse it, at any rate in the cold, since the solution remains clear. The boiling-point of this substance is more than 200° above that of the corresponding compound of arsenic.

Antimony trichloride, SbCl$_3$, once called 'butter of antimony,' can be obtained by dissolving antimony trisulphide in concentrated hydrochloric acid:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S \uparrow,$$
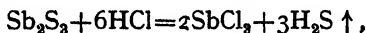
but is best prepared by the action of chlorine on antimony, which proceeds vigorously at ordinary temperatures. The pentachloride is usually produced at the same time; this is reduced by boiling the product with powdered antimony, and the trichloride is then purified by distillation, which may be followed by recrystallization from carbon disulphide.

Antimony trichloride is a colourless, very hygroscopic solid which absorbs water from the air to form a turbid liquid containing various oxychlorides. By treating it with a suitable quantity of water the oxychloride SbOCl can be obtained; this is, however, soluble in hydrochloric acid:

$$SbO' + H' \rightleftharpoons Sb''' + OH',$$

and antimony trichloride dissolves in the concentrated acid unchanged. From its concentrated aqueous solutions it can also be recovered by evaporation. It forms complexes with one, two, or three molecules of ammonia per molecule of trichloride, and with numerous other substances. The density of its vapour shows it to have the formula SbCl$_3$.

Antimony pentachloride, SbCl$_5$, is obtained by the action of

chlorine on the metal or the trichloride. The excess of chlorine is removed by a current of dry air and the product purified by distillation in a vacuum. It is a colourless, very hygroscopic liquid which fumes in the air. With a little water it forms a crystalline hydrate, $SbCl_5.H_2O$, from which the water can be removed by careful heating under reduced pressure, but it is irreversibly hydrolysed by excess of water. Like phosphorus pentachloride, it suffers on heating a reversible dissociation into the trichloride and chlorine. This takes place considerably below the boiling-point, but the pentachloride can be distilled unchanged at 60°–70° under low pressure. With chloride solutions it forms stable complex ions $SbCl_6'$, and the corresponding salts, such as $KSbCl_6$, are called the chloroantimonates.

Antimony tri-iodide, SbI_3, is obtained by treating a carbon disulphide solution of iodine with excess of antimony, filtering and evaporating the solution. It occurs in three different crystalline forms, of which two are yellow and one red. When heated in the air it loses iodine and forms an oxyiodide. It is decomposed by water, but dissolves without change in solutions of hydrogen iodide, and is soluble in various organic liquids, from which it can be recrystallized. In certain solvents the tri-iodide is associated, but its vapour density corresponds with the simple formula SbI_3.

Oxyhalides.—Of the numerous known *oxyhalides* of antimony, only *antimonyl chloride,* $SbOCl$, will be mentioned here. It is a white crystalline substance, insoluble in water but soluble in certain organic liquids, and is obtainable by treating antimony trichloride with a carefully regulated quantity of water:

$$SbCl_3 + H_2O \rightleftharpoons SbOCl \downarrow + 2HCl.$$

The reaction is reversible, and this compound strongly resembles bismuth oxychloride (p. 660).

ANTIMONY SULPHIDES.—Antimony forms a well-defined trisulphide, Sb_2S_3, and also a pentasulphide, Sb_2S_5, but the existence of a tetrasulphide, Sb_2S_4, is uncertain.

Antimony trisulphide, Sb_2S_3, occurs in nature as stibnite, the principal ore of antimony. It can be artificially prepared by heating the elements together or by the action of hydrogen sulphide on a hot solution of the trioxide in hydrochloric acid. If the solution is made very weakly acid (e.g. with acetic acid) and is dilute, a colloidal solution is obtained. The precipitation is reversible:

$$2Sb''' + 3H_2S \rightleftharpoons Sb_2S_3 \downarrow + 6H',$$

and antimony trisulphide, which is rather more soluble than arsenic trisulphide, has been used as a source of pure hydrogen sulphide.

The precipitated sulphide is an orange-red amorphous substance,

but if heated to over 200° in the absence of air it undergoes a change and becomes black and crystalline. It melts at 520° and boils at 1180°, but burns if strongly heated in the air or in oxygen. Like arsenic trisulphide, which it much resembles, it is slowly decomposed by boiling water and dissolves in sulphide solutions or in caustic alkalis. The products are called *thioantimonites*.

Antimony pentasulphide, Sb_2S_5, is precipitated by hydrogen sulphide from solutions of antimony pentoxide in hydrochloric acid of carefully chosen concentration (12 per cent), cooled to —20° in a freezing mixture. The product of this reaction contains not only the pentasulphide, but also free sulphur, removed by carbon disulphide. It is a brilliant yellow, orange, or brown powder, which on warming (70°) forms lower sulphides and releases sulphur, a property making it a useful vulcanizing agent for rubber, which assumes the familiar red colour.

ANTIMONY SALTS.—The basic properties of antimony trioxide are not strong, and antimony forms soluble salts only with the anions of the strongest acids; they are all hydrolysed in solution. No quinquevalent salts are known, the pentahalides being unmistakably covalent.

Antimony sulphate, $Sb_2(SO_4)_3$, can be obtained by dissolving the trioxide in hot concentrated sulphuric acid and cooling. The colourless crystals are washed free from acid with xylene. The crystals are deliquescent and are hydrolysed in the cold to a basic sulphate and by boiling water to the trioxide and sulphuric acid. By carefully regulated hydrolysis in the cold, *antimonyl sulphate*, $(SbO)_2SO_4$, can be obtained (compare antimonyl chloride). It is a white powder, insoluble in water, but soluble, as might be expected, in acids.

Antimony nitrate, $Sb(NO_3)_3$, cannot be prepared in aqueous solution, since it is decomposed by water, but can be obtained by mixing acetone solutions of silver nitrate and antimony trichloride.

Detection and Estimation of Antimony.—Many compounds of antimony, though not so deadly as those of arsenic, are yet powerful poisons, and the detection of traces of this element is of great importance. If arsenic is absent, Marsh's test can be used. Several methods are available for the separation of antimony from arsenic and other elements. One of the best is to dissolve the mixed sulphides of antimony and arsenic in a solution of sodium sulphide, and to precipitate the antimony from this solution as sodium antimonate by the addition of caustic soda and hydrogen peroxide:

$$Sb_2S_3 + 3S'' = 2SbS_3'''.$$
$$2SbS_3''' + 2Na^{\cdot} + 8H_2O_2 = 2NaSb(OH)_6 \downarrow + 6S \downarrow + 4OH'.$$
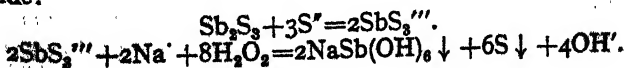
Alcohol is added to the liquid to reduce the solubility of the precipitate. If other metals are absent, antimony is usually precipitated from slightly acid solution by hydrogen sulphide as the trisulphide, and this is converted to the black crystalline form by heating at 300° in a stream of carbon dioxide; it is then weighed.

BISMUTH

Bi=209·00. *Atomic Number*, 83

History.—Bismuth was unknown to the ancient chemists, or, if known, was considered to be a kind of lead. The name *wismath* was given by RULANDUS (*Lexicon Alchemiae Rulandi*, Frankfort, 1612) to a certain metallic sulphide, but the name was afterwards applied to a new element, bismuth. 'Wismath' is derived from *wis mât* or *weisse Masse*, white mass or metal; the *w* was changed into *b* for the purpose of writing the name in Latin, from the alphabet of which language the letter *w* is missing. Bismuth and its compounds were studied by PARACELSUS and AGRICOLA, and more especially by BASIL VALENTINE, but BERGMAN (eighteenth century) first carefully distinguished between it and antimony, tin, and lead. The French chemist LÉMERY (1694) considered that bismuth was not a distinct metal, but that it could be obtained from arsenic and tin. It was GEOFFROY (1753) who first definitely proved that bismuth is a specific substance with certain similarities to lead.

Occurrence and Extraction.—Bismuth is not one of the commoner elements, though it occurs in small quantities in many parts of the earth. The principal deposits of bismuth are in Bolivia, where the metal is found native and associated with tin. The ores are concentrated by washing, and a considerable proportion of the 'concentrate' so obtained is shipped to European ports for extraction. Ores containing the native metal are usually treated by liquation, that is, the ores are heated with or without the addition of a flux (sodium carbonate and lime), and the molten metal is run off at the bottom. Its purity depends greatly on the nature of the ore, and it is usually necessary to refine it by one or more further ignitions with suitable fluxes. The preparation of pure bismuth in the laboratory is a difficult task, on account of the tenacity with which small quantities of lead and arsenic are retained, most undesirable impurities if the product is to be put to medicinal use. Several methods are available, most of them relying on the precipitation of the bismuth either as the basic nitrate or the oxychloride. Alternatively, the bismuth is precipitated as hydroxide, and this is dissolved in excess of caustic soda solution containing

glycerol. Easily reducible metals are now removed and filtered off by the addition of sugar (a reducing agent) in the cold; the bismuth is precipitated only on boiling. The product is melted with potassium cyanide, to prevent oxidation, and then forms a coherent mass of the pure metal.

Elementary Bismuth.—Bismuth is the only element of the series P—As—Sb—Bi not to display allotropy. It is a lustrous soft white metal with a density of 9·8; it melts at 271° and boils at 1560°. The density of the vapour (which is green in colour) corresponds with a monatomic molecule at high temperatures, but some association takes place near the boiling-point.

Bismuth is stable in cold air, whether moist or dry, but if heated it forms a surface coating of oxide, and if very strongly heated in air or oxygen it can be made to burn. Its standard electrode potential is probably intermediate between those of arsenic and antimony, i.e. about +0·2 volt, and it is unaffected by acids except in so far as they are also oxidizing agents. It will dissolve in hot concentrated sulphuric acid, which it reduces to sulphur dioxide, or in nitric acid, but in the concentrated acid is assumes the passive state (p. 423). Bismuth combines with the halogens, but a good deal less vigorously than does arsenic or antimony.

The metal is used in fusible alloys, in which it is often associated with tin, lead, and antimony: these alloys are used in electric fuse-wire and in automatic sprinklers designed to extinguish fires. As bismuth expands on solidification, its alloys are much used for casting type-metal. Bismuth is one of the elements of highest atomic number whose compounds are non-poisonous: an insoluble bismuth salt is therefore given to patients before examination by X-rays of the digestive tract.

Bismuth hydride, formula unknown, probably BiH_3, is the most difficult of all the hydrides of the nitrogen-bismuth group of elements to prepare. After many unsuccessful attempts had been reported, PANETH, by the radioactive indicator method, showed that such a compound did exist, and was able to work out a method for preparing identifiable quantities of it. An alloy of bismuth and magnesium, obtained by heating these elements together in a current of hydrogen (compare antimony hydride), is treated with a not too dilute acid in Marsh's apparatus, containing zinc and hydrochloric acid, and a stain resembling that produced by antimony is found in the heated tube. Alternatively the gaseous hydride may be collected in a condenser cooled with liquid air. The yield obtained is, however, too small for a thorough examination of the properties of this substance to be made.

OXIDES AND HYDROXIDES.—Bismuth forms a well-defined oxide, Bi_2O_3, but the existence of higher oxides is still uncertain. Unlike

the corresponding oxy-compounds of other members of the group, bismuth hydroxide is devoid of acidic properties.

Bismuth trioxide, Bi_2O_3, is the product of the combustion of bismuth in air, but is more conveniently obtained by strongly heating the basic nitrate or carbonate. If, however, the temperature rises too high—e.g. above 700°—the oxide melts and then attacks porcelain. It can also be obtained by heating the *trihydroxide*, $Bi(OH)_3$, precipitated from bismuth solutions by caustic alkalis. As, however, this process usually leads to the inclusion of a little basic salt in the precipitate, it is best to use a solution of the basic nitrate to which glycerol or mannitol has been added. From such a solution caustic alkalis precipitate the pure base.

Bismuth trioxide is a yellow solid which darkens on heating. It can without difficulty be reduced to the metal by heating in hydrogen. It is insoluble in water, but it dissolves in acids to form bismuth or bismuthyl salts. It remains completely unaffected by even concentrated solutions of the caustic alkalis, and no trace of acid function can be detected. The trihydroxide is a colourless substance which is converted to the oxide not much below 600°.

Bismuth tetroxide, Bi_2O_4, is obtained by oxidizing the trioxide, suspended in boiling concentrated caustic potash, with potassium ferricyanide. The product is washed with boiling dilute nitric acid, and dried by heating. It is a dark-coloured substance and has oxidizing properties: it will liberate chlorine from hydrochloric acid.

Bismuth pentoxide, Bi_2O_5. When in place of potassium ferricyanide chlorine is used as oxidant acting upon bismuth trioxide suspended in concentrated alkali solution, the product is an orange-coloured insoluble powder, commonly called a ' bismuthate,' but little is known with certainty about its composition. It has been asserted, but not confirmed, that a pentoxide Bi_2O_5 can be obtained from it by treatment with acid. 'Bismuthates,' however, certainly contain some powerful oxidant, converting, for example, manganous salts in nitric acid solution to permanganic acid at ordinary temperature, and they are used for this purpose in the determination of manganese in steel.

HALIDES.—Bismuth reaches the quinquevalent state less readily than either arsenic or antimony, and the pentafluoride is the only known pentahalide. Bismuth forms, however, a number of organo-compounds of the general type $(C_6H_5)_3BiX_2$, where X represents various anions. All the bismuth trihalides are known and stable. Claims to have prepared an oxide and halides of bivalent bismuth seem not to be well founded. The trihalides are solids, and are much less volatile and more salt-like than their arsenic and antimony analogues; excepting the trifluoride they are hydrolysed by much

water—but can form stable solutions in acids. Bismuth, unlike the other members of the subgroup, fails to yield halogeno-complexes of the type $(MX_6)^-$; all attempts to prepare $KBiF_6$ have been unsuccessful.

Bismuth pentafluoride, BiF_5. Bismuth trifluoride absorbs fluorine rapidly at 500°, and the pentafluoride sublimes as colourless needles, being more volatile than the lower fluoride owing to its covalent constitution. It reacts with water violently, yielding the trifluoride and some ozone. The composition was confirmed by reduction to bismuth in hydrogen, which is rapid at 150°. The vapour density has not yet been observed.

Bismuth trifluoride, BiF_3, is obtained by dissolving the trioxide in hydrofluoric acid, or can be precipitated by soluble fluorides from solutions of bismuth nitrate in dilute nitric acid (the acid is necessary to prevent hydrolysis of the nitrate). It is a colourless solid which can be fused without decomposition, and is the only halide of the subgroup to be insoluble in water, by which it is unaffected even on boiling.

Bismuth trichloride, $BiCl_3$, is obtained by heating bismuth in a stream of dry chlorine, when the trichloride condenses in the cold part of the apparatus. Alternatively it may be prepared by dissolving the trioxide in concentrated hydrochloric acid. The solution is evaporated to dryness and the trichloride is distilled off in a current of carbon dioxide. It is a colourless crystalline substance which melts at 233° and boils at 447°; its vapour density shows it to have the normal molecular weight. It is very hygroscopic, and when added to a large quantity of water is hydrolysed with the formation of the oxychloride $BiOCl$:

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

but dissolves unchanged in sufficiently concentrated hydrochloric acid. It is also soluble in hydrocarbons and other organic liquids and can be recrystallized from them.

Bismuth tribromide, $BiBr_3$, is obtained by the action of excess of bromine on bismuth, and is purified by distillation. It is a yellow crystalline substance, melting at 220° and boiling at 453° without decomposition to form a deep red vapour. Its behaviour with water is similar to that of the trichloride.

Bismuth tri-iodide, BiI_3, is obtained by heating the elements together. The excess of iodine is then driven off in a current of carbon dioxide and the tri-iodide is purified by distillation. It forms black crystals which melt at 439°. It is hydrolysed by water, but only very slowly in the cold, and it dissolves in acids to give a brown solution.

OXYHALIDES.—With all the halogens bismuth forms oxyhalides

of a type which may be represented by the best-known member, BiOCl. They can be prepared by the hydrolysis of the trihalides, since they are all insoluble in water, but the stability of the trifluoride towards water precludes this method of preparation, and the oxyfluoride must be obtained by the carefully regulated action of hydrofluoric acid on the trioxide.

Bismuth oxychloride, bismuthyl chloride, BiOCl, is precipitated when bismuth trichloride, or a solution of the trioxide in concentrated hydrochloric acid, is largely diluted with water. This reaction is often used for the detection of antimony and bismuth. The reaction is usually given as:

$$Bi^{...} + H_2O \rightleftharpoons BiO^{.} + 2H^{.},$$
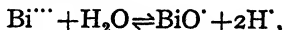
and is perfectly reversible, as the oxychloride is soluble in hydrochloric acid of sufficient concentration. A clear solution can be precipitated by dilution because three ions appear on the right-hand side of the equation but only one on the left; an equal fractional reduction of the concentration of all three therefore affects the value of the expression $\dfrac{[BiO^{.}]\,[H^{.}]^2}{[Bi^{...}]}$, and hence disturbs the equilibrium. The oxychloride is a white powder only slightly soluble in water and chemically unaffected by it even on boiling: it can be melted without decomposition.

Bismuth trisulphide, Bi_2S_3, is the only known compound of these two elements, the reported existence of sulphides of other compositions having proved illusory. It can be prepared either by heating the elements together or by precipitating a slightly acid solution of a bismuth salt with hydrogen sulphide; and in an impure form it occurs free in nature as *bismuthinite*. It is not among the most insoluble of the sulphides, and in very concentrated acid solution hydrogen sulphide at atmospheric pressure will not precipitate it.

It is a dark brown substance scarcely affected by heating in air, nor is it decomposed by boiling water. These properties distinguish it from the trisulphides of arsenic and antimony, and in analysis it is easily separated from them by its insolubility in dilute sulphide solutions, though if the solutions are concentrated some bismuth trisulphide dissolves to form a thiobismuthite. These compounds are much less stable than the corresponding thioantimonites or thioarsenites, and the soluble members are decomposed by water, so they are usually made either from very concentrated sulphide solutions or by fusing bismuth trisulphide with other sulphides.

THE BISMUTH ION.—The ion $Bi^{...}$ so readily undergoes hydrolysis, with the formation of bismuthyl compounds, that it can exist only

in acid solutions; but a number of bismuth salts have been prepared in the dry state, as well as a series of bismuthyl salts. The latter are insoluble in water but soluble in acids.

Bismuth sulphate, $Bi_2(SO_4)_3$, is prepared by evaporation of a solution of the trioxide in concentrated sulphuric acid. It consists of colourless crystals which can be heated to 400° without decomposition. The salt is very hygroscopic, and with water forms *bismuthyl sulphate*, $(BiO)_2SO_4$, a compound which can also be prepared by heating it strongly:

$$Bi_2(SO_4)_3 = (BiO)_2SO_4 + 2SO_3 \uparrow.$$
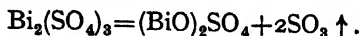
It is a colourless powder insoluble in water but soluble in acids.

Bismuth nitrate, $Bi(NO_3)_3.5H_2O$, is obtained by dissolving the trioxide in hot nitric acid and cooling the solution, but it is impossible to remove all the water from this salt, either by heating or in a vacuum desiccator, without decomposing it. It is freely soluble in nitric acid, but if the solution is diluted a basic nitrate of variable composition is thrown down. The name *bismuthyl nitrate* is given to the compound $BiONO_3.2H_2O$ obtained by gently heating the normal hydrated nitrate.

Bismuthyl carbonate, $(BiO)_2CO_3$, can be precipitated by carbonate solutions from solutions of bismuth nitrate in which hydrolysis has been prevented or reduced by the addition of mannitol, with which bismuth probably forms a complex. Bismuthyl carbonate decomposes on heating:

$$(BiO)_2CO_3 = Bi_2O_3 + CO_2 \uparrow.$$
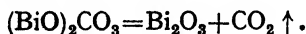
Bismuth phosphate, $BiPO_4$, can be precipitated by adding a soluble phosphate to a solution of bismuth nitrate in dilute nitric acid. This is one of the least soluble salts of bismuth and is consequently scarcely affected even by boiling water, nor will it dissolve in acids.

SUBGROUP A

VANADIUM, NIOBIUM, AND TANTALUM

VANADIUM

$V = 50.95.$ *Atomic Number,* 23

History.—Vanadium was discovered in 1830 by SEFSTRÖM in a Swedish iron ore, and was given the name which it now bears after Vanadis, a goddess of Scandinavian mythology. It was subsequently shown that the same element had been discovered some

thirty years before by DEL RIO, who, however, on further investigation had come to the conclusion that no new element was present in the Mexican mineral on which he had based his claim.

Occurrence and Extraction.—The quantities of vanadium extracted from its ores are still comparatively small, though the element is now known to be comparatively abundant: more abundant, for example, than copper.

The principal source of vanadium is *patronite*, a mixture of vanadium sulphides found in Peru. This is mixed with a flux and roasted in a reverberatory furnace, when the vanadium passes into the slag, which is then reduced to *ferro-vanadium* in a blast furnace. The 'acid extraction' process has also been widely used, particularly for the poorer deposits. In this process the ore is crushed and heated with fairly dilute sulphuric acid at 200° under a pressure of fifteen atmospheres. The solution is then filtered and evaporated to dryness: the product contains the vanadium and is heated strongly to convert it to the oxide. It is mixed with sodium carbonate, roasted in the air, and dissolved in hot water, from which carbon dioxide will precipitate any aluminium as oxide. Sodium vanadate can be obtained from the solution by concentration.

Elementary Vanadium.—In the early researches of BERZELIUS, the oxychloride $VOCl_3$ was mistaken for the chloride, and the oxide VO for the element. The preparation of vanadium presented unusual difficulties that have not yet been completely overcome; the metal forms oxides and nitrides of great stability from which it cannot easily be extracted. A 95-per-cent product can be obtained from the pentoxide and aluminium powder by the GOLD-SCHMIDT process, and a somewhat purer substance by reducing the chlorides with hydrogen, sodium, or sodium hydride. Attempts to prepare the metal by electrolysis of aqueous solutions of its compounds have been unsuccessful.

Vanadium is a grey lustrous metal with a density of about 6; it is the hardest of all metals. It melts at 1720°. It is oxidized by heating in the air, and burns if heated in oxygen, but it is quite unaffected by water. Among the acids, only hydrofluoric acid and the oxidizing acids will dissolve it. It will combine directly with chlorine, nitrogen, silicon, and other elements.

Some nine-tenths of the world's output of vanadium come into commerce in the form of ferro-vanadium. The addition of vanadium to steel increases the toughness and the tensile strength, and such steel is used in high-speed tools and the parts of machinery—e.g. of motor cars—which have to withstand frequent shock. The vanadium is added, in a proportion of less than 2 per cent, as a ferro-vanadium containing between 25 per cent

and 50 per cent of the element, usually prepared by the thermit process.

VANADIUM COMPOUNDS.—Vanadium has well-marked valencies of two, three, four, and five, and all the corresponding oxides are known.

Vanadium dioxide, VO, is prepared by heating an intimate mixture of the trioxide with vanadium to a high temperature, and is insoluble in water but soluble in acids, with which it yields violet solutions of hypovanadous salts, containing the bivalent cation V¨. These solutions can also be prepared from solutions of other vanadium compounds by reduction with sodium amalgam or at a cathode, and the hydroxide $V(OH)_2$ can be precipitated from them by the addition of caustic alkalis. The oxidation potential of the change V˙˙˙→V˙˙ is —0·2 volt, and the hypovanadous compounds, in which the element is bivalent, are among the strongest of reducing agents— compare the bivalent compounds of the adjacent element chromium. In acid solution they fairly rapidly evolve hydrogen, and even the insoluble hydroxide slowly decomposes water. They have been used in the dearsenification of commercial hydrochloric acid, as they will reduce arsenic chloride to arsenic, which can be filtered off.

Vanadium trioxide, V_2O_3, is obtained by reducing the pentoxide with hydrogen at a moderate temperature. It is a black substance with a very high melting-point, and burns when heated in the air: it will dissolve only in the oxidizing acids. Solutions of vanadous salts, in which vanadium is tervalent, must therefore be obtained by reduction of solutions of other vanadium compounds, and this can be carried out either electrolytically or with magnesium or zinc. The resulting solutions, which are green in colour, are powerful reducing agents which slowly decompose with the evolution of hydrogen, and are rapidly oxidized on exposure to the air. The insoluble hydroxide $V(OH)_3$ is precipitated from them by caustic alkalis.

Vanadium tetroxide, vanadyl oxide, V_2O_4, VO_2, (VO)O, is obtained by gentle reduction of the pentoxide; fusion with oxalic acid has been recommended. It is a dark blue solid of very high melting-point which absorbs oxygen from the air. It dissolves readily in acids to form solutions of vanadyl salts, containing the cation VO˙˙, and from these reactions derives its alternative name and formula, vanadyl oxide, (VO)O. Salts of quadrivalent vanadium usually decompose on heating into salts in which the metal is tervalent. Vanadyl solutions are blue, and can be prepared by gentle reduction of solutions of quinquevalent vanadium compounds, e.g. with hydrogen sulphide, sulphur dioxide, or even hydrogen. They are weak reducing agents. Vanadium tetroxide is amphoteric

Y

and has weak acidic properties; thus it will dissolve in caustic alkalis to form yellow solutions of *hypovanadates*, whose anion appears to be V_4O_9'':

$$2V_2O_4+2OH'=V_4O_9''+H_2O.$$
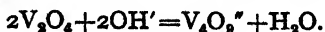
These yellow solutions are easily oxidized, even by the air, to colourless solutions of vanadates.

Vanadium pentoxide, V_2O_5, is the principal oxide of vanadium. It can be prepared by the ignition of ammonium metavanadate, NH_4VO_3, in an oxidizing atmosphere: a platinum crucible must be used.

$$2NH_4VO_3=V_2O_5+2NH_3\uparrow+H_2O\uparrow.$$
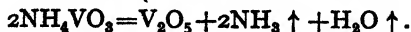
If it is required perfectly pure it is best to hydrolyse the oxychloride $VOCl_3$, finally heating the product with a little concentrated nitric acid. The pentoxide is a red or yellow substance which can exist in various forms. It melts at 690° and is stable towards heat, but at very high temperatures gives the trioxide and oxygen, and in the electric furnace can be reduced by hydrogen to the dioxide V_2O_2. It is insoluble in water, but a number of vanadic acids can be precipitated by acidifying vanadate solutions. The oxide is amphoteric, and will dissolve either in acids or in alkalis. Vanadic salts are oxidizing agents, and when the pentoxide dissolves in acids it often oxidizes them and dissolves as a vanadyl salt, e.g. with hydrochloric acid, chlorine and vanadyl chloride are obtained:

$$V_2O_5+6H^{\cdot}+2Cl'=Cl_2\uparrow+2VO^{\cdot\cdot}+3H_2O.$$

Vanadium pentoxide is used as a catalyst in the oxidation of sulphur dioxide (p. 683).

VANADATES.—These compounds are obtained by dissolving the pentoxide in alkaline solutions or heating it with bases. The vanadate ions bear some analogy of formula with the phosphate ions, but appear to differ from them by being mutually convertible in solution. Soluble orthovanadates, such as Na_3VO_4, can only exist in strongly alkaline solution: ' metavanadates ' contain the condensed anion V_4O_{12}''''. The vanadate ions are colourless.

Ammonium metavanadate, NH_4VO_3, one of the best-known compounds of vanadium, can be prepared by the addition of excess of ammonium chloride to vanadate solutions, and is purified by a succession of similar precipitations. It is a colourless substance only moderately soluble in water, and when strongly heated yields the pentoxide.

Sodium orthovanadate, Na_3VO_4, is obtained by fusion of the pentoxide with sodium carbonate, followed by recrystallization. Numerous colourless hydrates can be prepared from its solutions.

Pervanadates.—Vanadium resembles its neighbours titanium and chromium in forming coloured solutions when the vanadates are

acidified and treated with hydrogen peroxide. Solutions of the pervanadates are red and are fairly stable: they constitute a sensitive test for the presence of vanadium. Salts such as *potassium pervanadate*, KVO_4, can be prepared from solutions of the alkali-metal metavanadates and hydrogen peroxide.

HALIDES.—The known halides of vanadium are shown in the table:

Fluorides	—	VF_3	VF_4	VF_5
Chlorides	VCl_2	VCl_3	VCl_4	—
Bromides	VBr_2	VBr_3	—	—
Iodides	VI_2	VI_3	—	—

THE KNOWN HALIDES OF VANADIUM

In addition to these many oxyhalides are known, of which several are soluble in water. The fluorides and chlorides may be briefly described.

Fluorides.—The action of fluorine on vanadium produces a mixture of substances, and the fluorides are more easily obtained by the action of anhydrous hydrogen fluoride on the chlorides or bromides.

Vanadium trifluoride, VF_3, is obtained by heating the trichloride in hydrogen fluoride. It is a greenish-yellow refractory substance insoluble in water.

Vanadium tetrafluoride, VF_4, is obtained in a similar way by the action of hydrogen fluoride on the cold tetrachloride. It is a brownish-yellow deliquescent solid which dissolves in water, and yields the tri- and pentafluorides on heating:

$$2VF_4 = VF_3 + VF_5.$$

Vanadium pentafluoride, VF_5, is obtained, together with the trifluoride, by heating the tetrafluoride in nitrogen at 650°, and collects as a white solid in the cooler parts of the apparatus. It sublimes at 111° and is soluble in water, but the solution suffers some hydrolysis with the formation of oxyfluoride. It is the only pentahalide of vanadium.

Chlorides. — *Vanadium dichloride, hypovanadous chloride*, VCl_2, the best known dihalide of vanadium, is obtained by heating the trichloride to a high temperature in a stream of nitrogen:

$$2VCl_3 = 2VCl_2 + Cl_2 \uparrow,$$

or by passing a mixture of the tetrachloride and hydrogen through a red-hot tube. It forms pale green crystals which volatilize unchanged at a high temperature (above 1000°), and readily absorb water or oxygen. The violet solutions have the properties already described.

Vanadium trichloride, vanadous chloride, VCl_3, is obtained by the decomposition of the tetrachloride at a moderate temperature:

$$2VCl_4 = 2VCl_3 + Cl_2 \uparrow.$$

The tetrachloride may be heated nearly to boiling while a current of dry carbon dioxide is blown through it to remove the chlorine. The trichloride remains as violet, very hygroscopic crystals, very soluble in water or alcohol. The aqueous solutions can equally well be prepared by dissolving the trihydroxide in hydrochloric acid. When strongly heated in an inert gas the anhydrous substance yields the dichloride and the tetrachloride, and at a high temperature it can be reduced to the metal in a current of hydrogen.

Vanadium tetrachloride, VCl_4, is obtained by the action of chlorine on vanadium or ferro-vanadium, or by the action of a mixture of chlorine and sulphur monochloride on the hot pentoxide. The product of these reactions can be purified by distillation, and is a dark brown viscid liquid freezing at $-26°$ and boiling at $154°$; it has a normal vapour density. It dissolves in water to form a blue solution of the oxyhalide, $VOCl_2$, and decomposes into the trichloride and chlorine, slowly at ordinary temperatures but more rapidly on heating.

Sulphides.—A *trisulphide*, V_2S_3, and a *tetrasulphide*, VS_4, are known. Neither of them is very soluble in acids, as such, but they can be brought into solution by strong oxidizing agents such a nitric acid or hot concentrated sulphuric acid, and they form oxides when heated in the air.

Vanadium trisulphide, V_2S_3, is a grey solid obtained by heating any oxide of vanadium to redness in a current of hydrogen sulphide.

Vanadium tetrasulphide, VS_4, is prepared by heating the trisulphide with sulphur. If more strongly heated in a vacuum or an inert gas, the tetrasulphide dissociates into the trisulphide and sulphur. Like pyrites, FeS_2, the tetrasulphide probably contains S_2 groups. It is the chief constituent of the ore *patronite*.

Sulphates.—*Hypovanadous sulphate*, $VSO_4.7H_2O$, is obtained by the electrolytic reduction of a solution of vanadyl sulphate in the absence of air, followed by concentration in a vacuum. It is isomorphous with ferrous sulphate, $FeSO_4.7H_2O$.

Vanadous hydrogen sulphate, $VH(SO_4)_2.4H_2O$, is prepared by the electrolytic reduction of a solution of vanadium pentoxide in dilute sulphuric acid, followed by precipitation with the concentrated acid. Its solutions are reducing agents whose use has been recommended in place of titanous solutions in volumetric analysis. They appear to be rather less sensitive to atmospheric oxidation.

Vanadyl sulphate, $VOSO_4.2H_2O$, is prepared by reduction with

sulphur dioxide of a solution of vanadium pentoxide in dilute sulphuric acid, followed by evaporation. It is a hygroscopic sky-blue substance.

Nitrates.—Nitric acid oxidizes vanadium compounds to the quinquevalent condition, and produces pale yellow solutions containing vanadoxyl nitrate, $VO_2(NO_3)$.

NIOBIUM AND TANTALUM

Nb$=92\cdot9$; *atomic number*, 41. Ta$=180\cdot9$; *atomic number*, 73

History.—The history of *niobium* is peculiar. It was discovered in 1801 by HATCHETT in a sample of iron-ore from Massachusetts, and was given the name *columbium*. In 1844 the German chemist ROSE announced the discovery of a new element in a Bavarian mineral, and named it niobium, but it was not till 1853 that niobium was proved to be identical with columbium. The two names are still used by chemists for the same element: columbium (symbol Cb) should have right of priority, but in this country at least niobium is more generally used. *Tantalum* was discovered in 1802 by EKEBERG in Scandinavia; the name has been said to refer to the tantalizing character of his researches.

Occurrence and Extraction.—Both niobium and tantalum are rare elements. For many years of no commercial importance, tantalum was one of the first metals to be used in the filaments of electric-light bulbs, though it has now been replaced by tungsten. Niobium has not yet been put to practical use.

The two elements almost always occur together, and invariably as niobates and tantalates: the principal deposits are in Australia, where the metals occur as *tantalite*, a mixed niobate and tantalate of ferrous iron, with some manganese. The treatment of this substance is difficult, as it is unaffected by the common acids, excepting hydrofluoric acid. It is mixed with excess of potassium hydrogen sulphate and fused in an iron vessel, cooled, and extracted with water. The residue is then treated successively with ammonium sulphide and hydrochloric acid. The solid is dissolved in hydrofluoric acid and boiled to remove silica as the tetrafluoride. After concentration the solution is treated with potassium hydrogen fluoride, which deposits potassium fluotantalate, K_2TaF_7, but leaves the niobium in solution, from which it can be recovered, by further evaporation, as potassium oxyfluoniobate, $K_2(NbO)F_5.H_2O$.

Metallic tantalum can be prepared by electrolysis of potassium fluotantalate in a magnesia crucible with tantalum electrodes. It has also been prepared by a modification of the thermit process, using the pentoxide and a more energetic reducing agent than

aluminium, namely 'Mischmetal' (p. 597). Niobium can be prepared in a similar way. The separation of the compounds of the two elements beyond the point already described always offers great difficulties on account of their close resemblance, and is not attempted on the commercial scale. One successful laboratory process depends on the fact that tantalic acid is weaker than niobic acid, and can be precipitated from tantalate solutions by carbon dioxide in the cold, whereas niobates are unaffected by this treatment.

The resemblance of niobium and tantalum exceeds that of the neighbouring Group VI elements molybdenum and tungsten, but not that of the Group IV elements zirconium and hafnium.

Metallic Niobium and Tantalum.—These are both hard grey metals. Their densities are respectively 7·3 and 16·6, and their melting-points 1950° and 3027°. They are oxidized when strongly heated in the air, and some nitride may also be formed, but at ordinary temperatures they are unaffected by moisture. They combine with fluorine in the cold, and with the other halogens on heating. Among the acids, hydrofluoric acid is the only efficient solvent for these metals, and unless it is heated even this substance acts only slowly: they are also slightly affected by boiling concentrated sulphuric acid.

The use of tantalum in the filaments of incandescent lamps was due to its very high melting-point, in which, however, it is surpassed by tungsten. Its hardness makes it useful for certain cutting tools, and on account of its resistance to chemical attack it has been used as a substitute for the more expensive platinum in the manufacture of chemical apparatus. Its hardness and resistance to corrosion have also led to its use for the manufacture of surgical instruments.

COMPOUNDS OF NIOBIUM AND TANTALUM.—In these elements the valency of five predominates. They both form stable acidic pentoxides, and a number of lower oxides which have not been thoroughly investigated. The only known fluorides are the penta-fluorides, and penta- and tri-chlorides of both elements are well characterized. In their highest valencies both elements yield oxy-halides of the type MOX_3.

Pentoxides.—These compounds are prepared from the fluo-tantalates and oxyfluoniobates as follows. After heating with concentrated sulphuric acid has volatilized all the hydrogen fluoride, the residue is treated with boiling water, which precipitates niobic or tantalic acid. Traces of sulphuric acid can then be removed by repeated washing, followed by ignition with ammonium car-bonate; this leaves the pure pentoxide. The pentoxides are also produced when the metals are burned in oxygen. They are

colourless, very stable solids which can be reduced to lower oxides by hydrogen only at very high temperatures and pressures, or not at all. They will not dissolve in any acid except hydrofluoric acid, but they can be brought into solution by fusion with the caustic alkalis, with the production of *niobates* or *tantalates*. The hydrated pentoxides, which may be called *niobic* and *tantalic acids*, can be prepared by precipitating solutions of these substances with acids, or by other methods—often by the hydrolysis of the halides or oxyhalides. They are insoluble in water but will dissolve in aqueous solutions of the caustic alkalis.

Perniobates and Pertantalates can be obtained in solution by the action of hydrogen peroxide and acids on solutions of the niobates and tantalates; the former are yellow, the latter colourless. These solutions are believed to contain the anions NbO_4' and TaO_4'.

Halides.—*Pentafluorides*, NbF_5 and TaF_5, are prepared by the action of fluorine on the elements. They are colourless solids, the melting-points being 73° and 97° respectively, and the boiling-points 217° and 229°. They are hygroscopic substances which are hydrolysed by water, but if soluble fluorides are added to solutions of the pentoxides in hydrofluoric acid, fluoniobates and fluotantalates such as K_2NbF_7 or Na_3TaF_8 can be prepared.

Pentachlorides, $NbCl_5$ and $TaCl_5$, are produced by direct combination of the elements, but are more easily prepared by heating a mixture of the pentoxide and carbon in chlorine. They are both pale yellow solids, the melting-points being 194° and 211°, and the boiling-points 241° and 242°. They fume in moist air from the production of hydrogen chloride, and are hydrolysed by water.

The lower chlorides are obtained by reduction of the pentachlorides or oxychlorides.

Tantalum dichloride, $TaCl_2$, can be prepared by heating tantalum pentachloride with lead, or sodium amalgam. It will liberate hydrogen from water.

Tantalum trichloride, $TaCl_3$, has been prepared by the reduction of the pentachloride with aluminium at a lower temperature than is required for the production of the dichloride. It is partially hydrolysed by water, but dissolves in the presence of acids to form a green solution stable in the absence of air, which oxidizes it.

Tetrachlorides of both niobium and tantalum have been reported but not thoroughly examined.

GROUP VI

[OXYGEN], SULPHUR, SELENIUM, TELLURIUM, CHROMIUM,
MOLYBDENUM, TUNGSTEN, URANIUM

O = 16·00 *atomic number*, 8   Cr = 52·01; *atomic number*, 24
S = 32·06 *atomic number*, 16   Mo = 95·95; *atomic number*, 42
Se = 78·96 *atomic number*, 34   W = 183·86; *atomic number*, 74
Te = 127·61 *atomic number*, 52   U = 238·07; *atomic number*, 92

$$[O]—S \Big\langle {Cr—Mo—W—U \atop Se—Te}$$
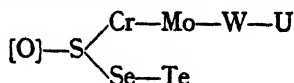
As in other groups near the ends of the table, the resemblances
between the subgroups are confined to compounds in which the
element has the group valency, in this case six, and the typical
elements form a natural series with the outer subgroup, in this
case Subgroup B. As the properties of oxygen and its compounds
have already been discussed (pp. 371–82), we shall first deal with
the series of elements sulphur, selenium, tellurium, and then with
Subgroup A.

Oxygen is an element whose properties are so important in our
system of chemistry that it is easy to lose sight of its periodic
relationships. In its invariable valency of two it resembles sulphur
more than any other element, but it is remarkable that in spite of
their higher molecular weight the compounds of sulphur in which
sulphur is linked to hydrogen are usually more volatile than the
corresponding compounds of oxygen.

SULPHUR, SELENIUM, TELLURIUM

This series of elements shows a well-marked gradation of pro-
perties, as is obvious from the following table, in which oxygen
has been included:

	Oxygen	Sulphur	Selenium	Tellurium
Atomic Number	8	16	34	52
Atomic Weight	16·00	32·06	78·96	127·6
Density (of solid)	1·43	1·96–2·06	4·28–4·80	5·93–6·4
Atomic Volume (appr.)	11	16	18	21
Melting-point	−219°	115°	217°	452°
Boiling-point	−183°	445°	688°	1390°

The elements are all non-metals which display allotropy. Since they have six electrons in the valency group they can complete their octets by forming bivalent anions, S'', Se'', Te''. The salts with the alkali-metals are all soluble, the others mostly insoluble. As with the halogens, the potential necessary to discharge the element from these anions decreases markedly as the atomic number increases. This operation is never difficult, and selenide or telluride solutions readily deposit the element when exposed to the air. Tellurium, the heaviest member, is the most metallic, but this characteristic is only very slightly developed.

The hydrides form a well-marked series. As the atomic number of the element increases they become less volatile and conspicuously less stable. They all have nauseous and rather similar odours. The heats of formation are (in calories):

$$H_2S, +5,280. \quad H_2Se, -18,500. \quad H_2Te, -34,100.$$
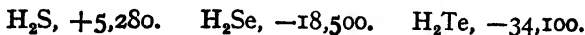
All the elements form oxyacids similar to sulphurous and sulphuric acids, but the relations between them are rather different, for while sulphurous acid is easily oxidized to sulphuric acid, selenic and telluric acids are fairly powerful oxidizing agents, which will, for example, liberate chlorine from hydrogen chloride. Telluric acid is unique in having a structure $Te(OH)_6$.

The variation in valency is most readily studied in the halides. In the hexafluorides of sulphur and selenium the covalency maximum of the element (p. 346) is displayed, and these halides are accordingly unaffected by water, which hydrolyses tellurium hexafluoride. In addition to hexafluorides the elements all form tetrahalides whose stability increases from sulphur to tellurium, and in these two electrons must be inert. Indeed all three elements show in some at least of their compounds a stable valency of four. The tetrahalides of tellurium show a slightly salt-like character, and in favourable conditions can exist in solution. As might be expected, selenium resembles tellurium, the remaining element of the subgroup, rather more closely than it resembles the typical element sulphur.

SULPHUR

S=32·06. *Atomic Number,* 16

History.—Since it occurs in the elementary state, sulphur has been known from prehistoric times. Its importance in the development of chemistry has been described in the Historical Introduction.

Occurrence and Extraction.—Sulphur is an abundant element, though far less abundant than oxygen. It occurs in large quantities

in many parts of the world as sulphides or sulphates and as the native element. Sulphur deposits are usually found in regions of volcanic activity, and the most important sources of sulphur are the deposits of Louisiana and Texas, in the United States, and of Sicily. The Louisiana deposits have been worked by an improved method since about 1903. The problem of the extraction of these deposits was a difficult one, as they were covered by some five hundred feet of soft sand and water. It was brilliantly solved by FRASCH, who devised the process now worked. A triple tube a foot in diameter is sunk to the bottom of the deposit. Down the inner tube is forced hot compressed air, and down the outer annular space water superheated to 180° under a pressure of ten atmospheres. The hot water melts the sulphur, which collects in a pool at the bottom of the well, and is blown up the middle annular space mixed with air, as a froth. The hot air on the inside of this tube and the hot water on the outside prevent its solidification on the way up. At the top the liquid sulphur is run into cooling trays, where it solidifies and is broken into lumps. It is very pure (about 99·9 per cent).
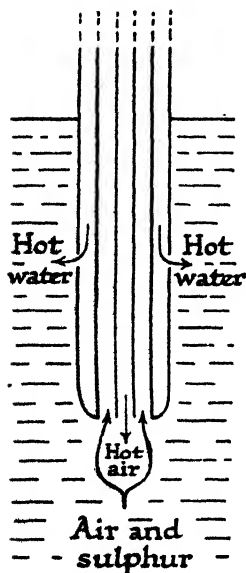
FIG. 134. SULPHUR WELL

In the Sicilian deposits the sulphur is near the surface, but is mixed with rock and other impurities which make it necessary to purify it by distillation. The heat for the process is provided by burning some of the sulphur to sulphur dioxide. It is doubtful whether Sicilian sulphur can compete on equal terms with the Louisiana product, and more than 80 per cent of the world consumption of elementary sulphur is now supplied by the United States. It is, however, possible that labour costs in Italy may be sufficiently reduced to bring Sicilian sulphur back to its predominant position as far as Central Europe is concerned.

Properties.—Sulphur occurs in more allotropic forms than any other element: we shall discuss only a few of the more important. The density of the modifications differs slightly, but is always about 2.

1. *Rhombic, octahedral, or α-sulphur.*—This is the ordinary form of sulphur. It is stable at room temperature, and the other varieties revert to it more or less rapidly. It is also precipitated at room temperature from solutions of sulphur in such solvents as

carbon disulphide or chloroform. If *rapidly* heated it melts at 114·5°. It is bright yellow in colour. Rhombic sulphur crystals consist of S_8 molecules in puckered octagonal rings, 16 to the unit cell.

2. *Monoclinic or β-sulphur.*—This is the stable form of sulphur at temperatures between 94·6° (the transition-point) and its melting-point of 120°. It can be obtained by cooling liquid sulphur or by crystallizing sulphur from its solutions in this temperature interval, and, as is so often found, although metastable below 94·6°, yet it often appears first when sulphur is crystallized from its solutions below this temperature. Under this condition it subsequently reverts to α-sulphur.
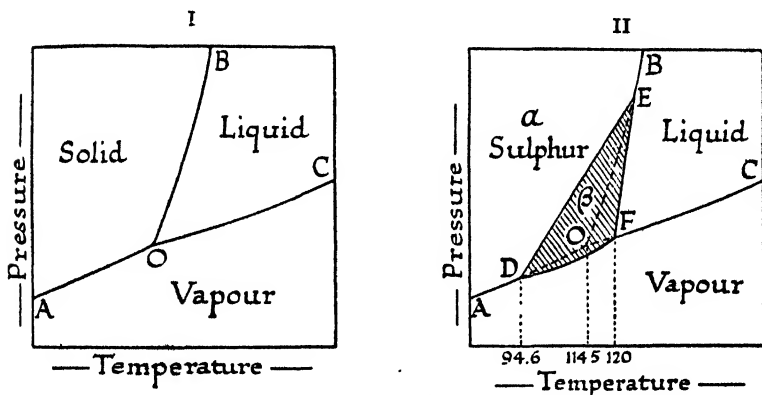
FIG. 135. EQUILIBRIUM BETWEEN α- AND β-SULPHUR

Figure I shows the usual pressure-temperature relations of a substance which, like sulphur, contracts on solidification, O being the triple point, and at a temperature very nearly equal to the melting-point under atmospheric pressure. Figure II shows how this simple type of diagram must be modified to provide for the occurrence of a second solid modification, in this case β- or mono-clinic sulphur. The figure is diagrammatic only. β-Sulphur is the stable variety within the shaded area; the diagram shows that it contracts, as α-sulphur does, on solidification (since its melting-point is raised by pressure), and that its melting-point is nearly 120°.

3. *Nacreous sulphur* is a modification resembling β-sulphur, from which it differs in its crystalline form, and may be obtained by cooling liquid sulphur under certain conditions or by producing sulphur in various chemical reactions such as the decomposition of polysulphides by acids.

4. *Plastic sulphur*, produced when molten sulphur is suddenly chilled by being poured in a thin stream into cold water. It is a sticky elastic substance which rapidly reverts to the rhombic form; it is in fact an undercooled liquid. It is known to consist of long chains or ' fibres ' of sulphur atoms. A form of sulphur insoluble in carbon disulphide may be obtained as residue by extracting plastic sulphur with carbon disulphide.

5. *Colloidal sulphur* can be obtained by the interaction of dilute solutions of hydrogen sulphide and sulphur dioxide. The solutions may be of various colours according to the size of the particles.

Sulphur is usually supplied to the laboratory either in lumps or in a fine yellow powder called *flowers of sulphur*, obtained by condensing sulphur vapour on a surface below its melting-point (see the phase diagram). Sulphur is distilled from a retort into a large chamber, on whose walls the flowers of sulphur collect. At temperatures not far above the melting-point molten sulphur is a mobile light brown liquid, but as the temperature is raised the liquid becomes black and viscous. At about 200° it is opaque and scarcely fluid, but on raising the temperature still further the fluidity is regained, and the liquid, though dark in colour, is transparent. These changes have now been fully explained. At temperatures near to 200° most of the eight-membered rings present in the solid and in the liquid near the melting-point become broken, and the fragments re-unite into very long chains of sulphur atoms. A high viscosity is characteristic of the presence of such chain molecules, and is due to their approximate alignment. The chains must be terminated by unsaturated sulphur atoms: they are in fact free radicals, albeit of very high molecular weight, and to this the deep colour is due. On suddenly chilling the chains persist and confer on plastic sulphur the elastomeric properties typical of rubber. At room temperature, however, most of the chains break up to give place to the original rings, but some sulphur of high molecular weight survives which is insoluble in carbon disulphide.

Liquid sulphur boils at 444·5°. As sulphur is easily purified by distillation this temperature is frequently used in the standardization of apparatus, such as thermocouples, for measuring high temperatures. Vapour-density measurements show that the sulphur molecule in the vapour phase at temperatures not far above the boiling-point is S_8. Measurements by the usual methods of the molecular weight of sulphur in its solutions lead to similar results. At higher temperatures the vapour dissociates into S_2 molecules, by fission of the cyclic S_8 molecules, and at 900° the vapour density corresponds with S_2. At about 2000° vapour-density measurements show single atoms to exist in the vapour.

Sulphur is a colourless or yellow substance which darkens

on heating. It is an excellent insulator, and is used for this purpose in electrical apparatus, e.g. in electroscopes. It combines with almost all elements either at room temperature or on heating. It is stable in the air, but on heating burns with a blue flame to form the gas sulphur dioxide, SO_2, and a little sulphur trioxide, SO_3. Sulphur is insoluble in water, and does not react with it, but when steam is passed through boiling sulphur a little hydrogen sulphide and sulphur dioxide are produced:

$$3S + 2H_2O \rightleftharpoons 2H_2S + SO_2.$$
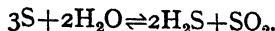
The reaction between sulphur and some metals, especially if both are in the powdered state, is very violent. Thus a mixture of zinc dust and flowers of sulphur becomes incandescent when touched with a red-hot bar. Gunpowder is a mixture of charcoal, sulphur, and potassium nitrate.

Sulphur will not dissolve in acids as such—i.e. it is unaffected by hydrogen ions—but it will dissolve in alkaline solutions, especially on heating. Sulphides and thiosulphates are among the products, but more complex substances are also produced. The simplest form of the equation is:

$$4S + 6OH' = 2S'' + S_2O_3'' + 3H_2O,$$
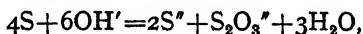
but it is incomplete.

The principal uses of sulphur are the preparation of sulphuric acid and calcium bisulphite. It is also used in dusting vines to preserve them from fungi, in valcanizing rubber, and in the preparation of carbon disulphide.

HYDRIDES.—**Hydrogen sulphide,** 'sulphuretted hydrogen,' H_2S, occurs naturally in certain volcanic gases, and is formed when hydrogen combines with molten sulphur or sulphur vapour:

$$H_2 + S \rightleftharpoons H_2S,$$
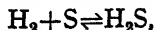
but as the reaction is reversible this is not a convenient method of preparation. In the laboratory the gas is usually prepared by the action of a dilute acid such as hydrochloric acid on a metal sulphide —usually ferrous sulphide—in KIPP's apparatus or similar device:

$$FeS + 2H^{\cdot} = Fe^{\cdot\cdot} + H_2S \uparrow.$$

It may be dried with calcium chloride. If ordinary ferrous sulphide is used, the gas is likely to contain hydrogen, hydrogen chloride, phosphine, and arsine. With the exception of the hydrogen these impurities may be removed by drying the gas with calcium chloride and passing it over iodine, which forms the iodides of phosphorus

and arsenic, and then washing it several times with water and drying again. Perfectly pure hydrogen sulphide can be prepared by the action of water on synthetic aluminium sulphide:

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S \uparrow .$$
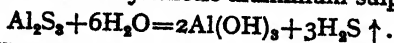
Properties.—Hydrogen sulphide is a colourless gas with an objectionable smell and highly toxic properties. It is a product of the decay of organic matter containing sulphur, and is therefore present in rotten eggs. It can be condensed to a liquid at $-6o°$. It is slightly soluble in water: at room temperature a solution of the gas saturated at atmospheric pressure is about one-tenth molar. The offensive odour of certain sulphur springs—such as those at Harrogate—is due to dissolved hydrogen sulphide. In a liberal supply of air hydrogen sulphide can be burned completely to sulphur dioxide and water:

$$2H_2S + 3O_2 = 2H_2O + 2SO_2,$$
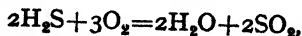
and can form explosive mixtures with air or oxygen, but if the supply of air is inadequate, sulphur vapour and water are produced:

$$2H_2S + O_2 = 2H_2O + 2S.$$
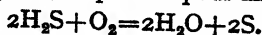
The presence of sulphur in a jet of hydrogen sulphide burning in the air can be demonstrated by applying it to a cold surface, such as that of a beaker full of cold water, on which sulphur will condense.

The gas is rather heavier than air: vapour density 17 (hydrogen $=1$). On heating it dissociates into its elements:

$$H_2S \rightleftharpoons H_2 + S,$$

but a very high temperature must be reached before dissociation is nearly complete.

When mixed with sulphur dioxide, hydrogen sulphide produces a cloud of sulphur:

$$2H_2S + SO_2 = 2H_2O + 3S,$$
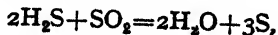
though the gases do not react if dry. It is easily oxidized to sulphur (and sometimes higher oxidation-products) by solutions of hydrogen peroxide, chromates or permanganates, by dilute nitric acid, or by concentrated sulphuric acid, which cannot therefore be used for drying it. It ignites spontaneously in contact with sodium peroxide. With chlorine, bromine, and iodine, sulphur and the halogen acid are produced:

$$H_2S + Cl_2 = 2HCl + S \downarrow .$$
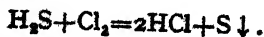
The aqueous solutions of hydrogen sulphide are slowly oxidized by the air with the production of sulphur. At low temperatures a solid hydrate, $H_2S.6H_2O$, can be isolated from them. Hydrogen sulphide in aqueous solution is a very weak acid: the dissociation-constant of the first dissociation, $H_2S \rightleftharpoons H^+ + HS'$, is about

10^{-7}, and of the second, $HS' \rightleftharpoons H^{\cdot} + S''$, about 10^{-15}, so that $\dfrac{[H^{\cdot}]^2[S'']}{[H_2S]} = 10^{-7}.10^{-15} = 10^{-22}$. As already explained (p. 195), hydrogen sulphide is much used in qualitative analysis for the separation of the elements into groups depending on the solubilities of their sulphides. The solubility-products of some insoluble sulphides (at 18°) are given below:

MnS (green), 6×10^{-22}; MnS (buff), 7×10^{-16}; FeS, about 10^{-20}; Tl$_2$S, 5×10^{-24}; ZnS, 10^{-25} to 10^{-26}; CoS, 2×10^{-27}; NiS, 10^{-27}; CdS, about 10^{-28}; PbS, 3×10^{-28}; CuS, 3×10^{-42}; Ag$_2$S, 10^{-50}; Hg$_2$S, 10^{-47}; HgS, 3×10^{-54}.

Hydrogen sulphide is poisonous to all forms of life.

Hydrogen persulphides.—Solutions of the soluble sulphides, i.e. those of the alkali- and alkaline-earth metals or of ammonium, readily dissolve sulphur, forming yellow solutions containing a divalent complex anion produced by the combination of a sulphide ion with neutral sulphur atoms. When such a solution is acidified in a freezing-mixture, a yellow oil settles to the bottom of the liquid which is a mixture of the higher sulphides of hydrogen. These can be separated by fractional distillation under reduced pressure into the *disulphide*, H$_2$S$_2$, and the *trisulphide*, H$_2$S$_3$. These are liquids which on keeping or warming readily decompose into hydrogen sulphide and sulphur. Their odours are more powerful even than that of hydrogen sulphide. Although polysulphides such as Na$_2$S$_5$ undoubtedly exist, no hydrogen persulphide containing a higher proportion of sulphur than H$_2$S$_3$ has been isolated.

Sulphides of the Metals.—These frequently occur in nature. They can be prepared:

(i) by direct combination—all metals except platinum and gold;
(ii) by heating oxides of metals in the vapour of carbon disulphide;
(iii) by precipitating a salt of the metal, made alkaline if necessary by ammonia, with hydrogen sulphide or ammonium sulphide. This method is not available for ammonium, the alkali-metals, or the alkaline-earth metals, whose sulphides are soluble, nor for beryllium, aluminium, or chromium, whose sulphides are too soluble to exist in the presence of water: the low solubility of the hydroxides of these three metals, and their weakness as bases, causes the immediate hydrolysis of their sulphides:

$$Al_2S_3 + 6H_2O \rightarrow Al(OH)_3 \downarrow + 3H_2S \uparrow.$$

The sulphides are solid substances, often strongly coloured, and with the exceptions noted are all more or less insoluble in water.

The valency of sulphur in the sulphides is always two, but per- or polysulphides are known as described above.   When treated with acids the sulphides may or may not liberate hydrogen sulphide. Taking a divalent metal as illustration, the equilibrium in the change:

$$MS \downarrow + 2H \cdot \rightleftharpoons H_2S \uparrow + M\cdot\cdot,$$
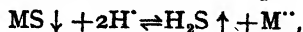
depends on the concentrations of the reactants and products, that is, on the solubility of the sulphide, the concentration of hydrogen ions provided by the acid, the solubility of hydrogen sulphide in water at the temperature and pressure selected, and the concentration of metal ions, if any, in the solution.   Thus the very insoluble mercuric sulphide is unaffected by cold concentrated hydrochloric acid, but with cold moderately concentrated hydriodic acid readily liberates hydrogen sulphide: this is because the concentration of mercuric ions in iodide solutions is smaller even than in chloride solutions (p. 515).   The solubility of aluminium hydroxide, on the other hand, is so small that the sulphide of this element is decomposed by water alone.

OXIDES AND OXYACIDS.—The most important oxyacids and oxides of sulphur are *sulphurous* and *sulphuric acids*, H_2SO_3 and H_2SO_4, and their anhydrides *sulphur dioxide*, SO_2, and *sulphur trioxide*, SO_3.   The remaining oxides are *sulphur sesquioxide*, S_2O_3, and *sulphur heptoxide*, S_2O_7, while the remaining acids include *hyposulphurous acid*, $H_2S_2O_4$, *thiosulphuric acid*, $H_2S_2O_3$, *chlorsulphonic acid*, $Cl.HSO_3$, a derivative of sulphuric acid, *perdisulphuric acid*, $H_2S_2O_8$, *permonosulphuric acid*, H_2SO_5, and a series of compounds called the *polythionic acids*.

Sulphur dioxide, SO_2, is prepared on a large scale in industry by burning sulphur in air or roasting pyrites; the gas from either source may contain a little sulphur trioxide, and when this is an undesirable impurity the sulphur is burned in a more limited supply of air in a special furnace.   Sulphur dioxide for sulphuric acid manufacture is recovered to an increasing extent from furnace gases evolved in certain industrial processes, e.g. the roasting of zinc sulphide.   In the laboratory the gas is procured either from a siphon (from which the liquid can also be obtained by inverting it), or by the action of copper on hot concentrated sulphuric acid.   In addition to cupric sulphate the residue contains cuprous sulphide, which colours it black, but the principal action may be written:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 \uparrow + 2H_2O.$$

Other substances may be used instead of copper for the reduction of the sulphuric acid.   Sulphur dioxide can also be made by the action of acids on sulphites, bisulphites, or thiosulphates, e.g.:

$$HSO_3' + H\cdot = H_2O + SO_2 \uparrow.$$
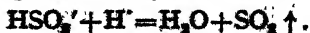
Properties.—Sulphur dioxide occurs in nature in the gases from volcanic vents and in certain springs, and it is liberated into the atmosphere of industrial areas by the combustion of the sulphur compounds contained in coal. Sulphur dioxide is inimical to human or plant life, and also causes stonework to decay. Steps are now being taken to reduce the quantity set free into the air from factory chimneys.

Sulphur dioxide is a colourless gas with an acrid taste and smell of 'burning sulphur.' Its vapour density is 32 (hydrogen$=$1), so it is more than twice as heavy as air, and can be collected by displacing air upwards. It boils at $-10°$ and can be condensed to a solid at $-72°$; the vapour pressure of the liquid at room temperature, as in a sulphur dioxide siphon, is nearly three atmospheres. The liquid scarcely conducts electricity. Sulphur dioxide will not burn, but it will combine with oxygen on the surface of a catalyst; the equilibrium conditions are discussed under *sulphur trioxide.*

Sulphur dioxide dissolves freely in water, which at room temperature and atmospheric pressure takes up about fifty times its own volume of the gas. The solubility does not obey HENRY's law except as a rough approximation, and the solution behaves as though it contained an acid—sulphurous acid, H_2SO_3. Conductivity measurements and potentiometric titration show this acid to be fairly strong in its first dissociation but weak in its second dissociation. Sulphurous acid can be titrated to a bisulphite with methyl red at a hydrogen ion concentration of about 10^{-5}, or to a sulphite with phenolphthalein at a hydrogen ion concentration of 10^{-9}; the dissociation-constant of the second dissociation, $HSO_3' \rightleftharpoons H^{\cdot} + SO_3''$, is about 10^{-7}. A hydrate, $SO_2.6H_2O$, can be obtained from the solutions at low temperatures, but the acid itself has never been isolated. Solutions of sulphur dioxide are slowly oxidized by the air to sulphuric acid:

$$2H_2SO_3 + O_2 = 2H_2SO_4,$$
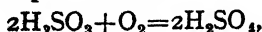
especially in the presence of certain salts which act as catalysts, and even if air be excluded a slow decomposition in the sense of the equation:

$$3H_2SO_3 = 2H_2SO_4 + S\downarrow + H_2O,$$

takes place.

On account of the ease with which sulphur dioxide in contact with water can be oxidized to sulphuric acid, the gas is a fairly powerful reducing agent, and will, for example, reduce iodine to an iodide, permanganates to manganous salts, and chromates to chromic salts. The reducing action can be represented:

$$SO_3'' + H_2O \rightarrow SO_4'' + 2H^{\cdot} + 2 \text{ electrons},$$
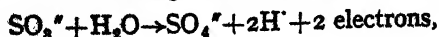
but the actual reducing agent is probably the ion $HSO_3{}'$, so that sulphur dioxide exerts a reducing power only in faintly acid solution. Weakly acid solutions of ferric salts are reduced by sulphur dioxide to the ferrous condition:

$$HSO_3{}' + H_2O + 2Fe^{\cdots} = SO_4{}'' + 3H^{\cdot} + 2Fe^{\cdot\cdot},$$
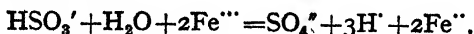
but in concentrated hydrochloric acid the reaction will not take place; indeed, in such a solution sulphur dioxide acts as an oxidizing agent and will oxidize ferrous salts to ferric salts:

$$SO_2 + 4H^{\cdot} + 4Fe^{\cdot\cdot} = S \downarrow + 2H_2O + 4Fe^{\cdots}.$$

Sulphur dioxide is used on the large scale for bleaching delicate fabrics, sponges, etc., but the colour usually returns after some time by atmospheric oxidation of the colourless compound (*leuco-base*) to which the colouring matter is reduced. Very large quantities of sulphur dioxide, usually prepared by burning pyrites, are used in the preparation of calcium hydrogen sulphite for the manufacture of paper from wood-pulp. The gas is passed through towers filled with limestone through which water trickles, and the action is:

$$2H_2SO_3 + CaCO_3 = Ca(HSO_3)_2 + CO_2 \uparrow + H_2O.$$
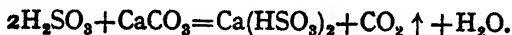
Sulphur dioxide is also used on the large scale as a disinfectant, as a reducing agent in organic chemistry, as the working liquid of refrigerators, and as an ' antichlor ' for removing chlorine from goods bleached with that substance:

$$SO_3{}'' + H_2O + Cl_2 = SO_4{}'' + 2H^{\cdot} + 2Cl'.$$

Sulphites.—Solutions of the sulphites of the alkali-metals are prepared by passing sulphur dioxide through solutions of their hydroxides, but with excess of sulphur dioxide the bisulphites or hydrogen sulphites are produced (compare carbon dioxide):

$$2OH' + SO_2 = SO_3{}'' + H_2O. \qquad SO_3{}'' + SO_2 + H_2O = 2HSO_3{}'.$$

Sulphites of other metals can be obtained by precipitation of a solution of a salt of the metal with sulphur dioxide or a soluble sulphite—e.g. silver sulphite, Ag_2SO_3, or barium sulphite, $BaSO_3$—or by dissolving the oxide or carbonate in sulphurous acid. Many of the insoluble sulphites will dissolve in excess of sulphurous acid as bisulphites (compare the carbonates), e.g.:

$$BaSO_3 \downarrow + H_2SO_3 = Ba^{\cdot\cdot} + 2HSO_3{}'.$$
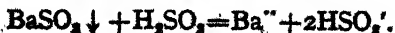
When treated with acids stronger than sulphurous acid the sulphites all yield sulphur dioxide, since at atmospheric pressure sulphurous acid cannot exceed a certain small concentration in water. The

precipitate produced with silver salts is soluble in excess of the sulphite solution, a complex ion being formed:

$$2Ag^{\cdot}+SO_3{''}\rightarrow Ag_2SO_3\downarrow. \qquad Ag_2SO_3\downarrow+SO_3{''}\rightarrow 2AgSO_3{'}.$$

Sulphites can easily be distinguished from thiosulphates by the precipitate of sulphur given by solutions of thiosulphates when treated with acids. The atmospheric oxidation of solutions of sulphites can be almost wholly prevented by the addition of traces of certain anti-catalysts (of which quinone is one of the most effective), and has been shown by RICE to be a heterogeneous reaction, since it is completely arrested, even in the presence of a positive catalyst such as a copper salt, by the removal of dust.

The constitution of the sulphite ion may be written as $^-O{-}S\Big\langle{\substack{O^- \\ O}}$

but the intervention of mesomerism (' resonance ') causes all the linkages between sulphur and oxygen to become identical (see p. 351). The anion has a pyramidal shape, with sulphur at the apex.

Sulphur trioxide.—Sulphur trioxide, SO_3, is produced in small quantities when sulphur burns in air or oxygen, and is made on a very large scale for the manufacture of sulphuric acid by the oxidation of sulphur dioxide with air at 450°. In the laboratory it may be prepared by the distillation of fuming sulphuric acid or of various sulphates, of which ferric sulphate is the most suitable:

$$Fe_2(SO_4)_3=Fe_2O_3+3SO_3\uparrow,$$
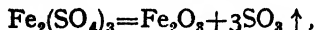
or by heating concentrated sulphuric acid with phosphorus pentoxide or concentrated phosphoric acid:

$$H_2SO_4-H_2O=SO_3\uparrow.$$

Sulphur trioxide exists in three forms: α-sulphur trioxide, which crystallizes in long needles at 17° and boils at 45°; β-sulphur trioxide, a substance with the appearance of asbestos, melting at 30°, into which the α-form spontaneously changes on keeping; and γ-sulphur trioxide, resembling the β-form in appearance, but with a much higher melting-point, obtained from the β-form by intensive drying. Since sulphur trioxide has a great affinity for water it is a self-drying substance, and therefore peculiarly suitable for experiments on intensive drying. The vapour pressures and melting-points depend on the previous history of the substance and on the degree of dryness to a most remarkable extent.

Sulphur trioxide fumes in moist air and dissolves in water with a hissing noise, producing sulphuric acid; it is indeed sulphuric anhydride. The reaction with water evolves much heat, and if incautiously conducted may lead to explosion.

Sulphuric acid, H_2SO_4, is required in almost all the chemical and allied industries, and is therefore manufactured on a very large scale; the total annual production amounts to some 10 to 14 million tons. During the eighteenth century, when it first acquired industrial importance, the supply of Nordhausen acid proved insufficient, and sulphuric acid was manufactured by burning a mixture of sulphur and saltpetre and collecting the gaseous products in water. Rapidly increasing demands led to great improvements in procedure, and the *lead-chamber* method was gradually elaborated by ROEBUCK and GARBETT (1746), LA FOLLIE (1774), CLÉMENT and DÉSORMES (1793), GAY-LUSSAC (1830), and GLOVER (1860). Since 1900 the lead-chamber process has had a serious rival in the *contact* process, suggested by PEREGRINE PHILLIPS of Bristol as long ago as 1831, but first successfully operated by R. KNIETSCH of the German firm Badische Anilin-und-Sodafabrik.

Both the lead-chamber and the contact process are catalytic, and both depend upon the oxidation of sulphur dioxide by atmospheric oxygen. The contact process yields a very pure and very concentrated acid, or oleum if required, but is rather more expensive to run than the lead-chamber process. On the other hand, the lead-chamber acid is less pure than the contact acid and cannot be economically concentrated or converted into oleum. Both processes are consequently employed, but the older method, while still producing the bulk of the world's output, is gradually being displaced by the contact method.

The sulphur dioxide required as raw material is obtained by the combustion in air of either sulphur:

$$S+O_2=SO_2;$$

or iron pyrites:

$$4FeS_2+11O_2=2Fe_2O_3+8SO_2;$$

or zinc blende:

$$2ZnS+3O_2=2ZnO+2SO_2;$$
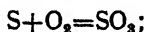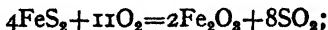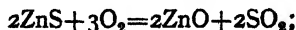
or the ' spent oxide ' of the gas works.

The United States and Italy, having large deposits of sulphur, mainly employ the first method; in England and Germany, however, iron pyrites, zinc blende, and spent oxide are generally used, though English manufacturers import a certain amount of sulphur for the purpose. Taking European practice as a whole, the principal source of sulphur dioxide is iron pyrites, which occurs in inexhaustible quantities in the Rio Tinto district of Spain and in smaller deposits in the U.S.S.R., Belgium, France, and Cyprus. Good quality pyrites contains 45 to 50 per cent of sulphur (FeS_2, when pure, contains 53 per cent), all of which is available on combustion.

The heat of combustion is so great that, once ignited, the pyrites continues to burn spontaneously. Zinc blende is poorer in sulphur (33 per cent when pure, usually about 20 per cent commercially) and requires a higher temperature with application of external heat for complete combustion. This disadvantage is offset by the fact that the residual zinc oxide is the chief source of zinc; indeed, the manufacture of sulphuric acid from blende is merely a subsidiary process in the extraction of zinc.

THE CONTACT PROCESS.—The essential reaction in this process is:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45,200 \text{ calories.}$$
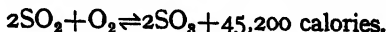
The sulphur trioxide is then combined with water to form sulphuric acid:

$$H_2O + SO_3 = H_2SO_4.$$
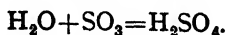
Consideration of the first equation will show that:

(a) The proportion of SO_3 in the equilibrium falls as the temperature rises (LE CHATELIER's principle). At 450°, the equilibrium mixture contains 98 per cent SO_3; at 550°, 85 per cent; at 620°, 70 per cent; at 700°, 40 per cent; and at 1,000°, practically nil.

(b) Conversion of SO_2 into SO_3 will be rendered more nearly complete by using an excess of oxygen (*mass action*). If the sulphur trioxide remains in the state of gas, the equation is:

$$\frac{[SO_3]^2}{[SO_2]^2[O_2]} = K.$$

(c) The forward reaction is accompanied by a decrease in volume and is therefore favoured by increase of pressure (Le Chatelier).

From these facts the best working conditions would appear to be: comparatively low temperature, increased pressure, and excess of oxygen (air). Unfortunately, however, the time taken to reach equilibrium even at 450° is much too great, while raising the temperature to a point at which the reaction takes place at a satisfactory speed causes the equilibrium proportion of sulphur trioxide to be negligibly small. It is clear that a solution of the problem lies in the discovery of a catalyst to accelerate the attainment of equilibrium at a temperature which gives a high yield of sulphur trioxide. Two such catalysts are commonly employed, viz. platinum, and vanadium pentoxide or silicate. Platinum is the more efficient, but its catalytic power is rapidly destroyed by the impurities—e.g. arsenious oxide—almost always present in commercial sulphur dioxide; hence careful purification of the gases has to be carried out if platinum is used. Vanadium pentoxide is less efficient, especially with gases in which the proportion of sulphur dioxide is low, but is unaffected by the impurities which 'poison' platinum. For this reason, it is

coming into general use, and newly built contact plants are almost all designed for vanadium catalysts.

In the presence of the catalyst, the reaction takes place quickly at 450°, and a 98 per cent yield of SO_3 is obtained. Excess of air is employed, in accordance with the mass-action requirement, but increased pressure is found to be unnecessary: in some works a pressure of 1·5–1·7 atmospheres is used.

Typical procedure in a modern works using sulphur as the raw material is as follows. Sulphur, from a steel hopper, is fed into a melter heated by superheated steam; any solid impurities are retained by a series of baffles. The molten sulphur is pumped into a burner consisting of a horizontal cylindrical steel tank lined with heat - resisting firebrick, and meets an incoming stream of air previously dried by passage through 94 per cent sulphuric acid. Complete combustion occurs, and the gases— which contain about 7 per cent of sulphur dioxide, with excess of air and nitrogen—leave the burner at a temperature of about 700°.
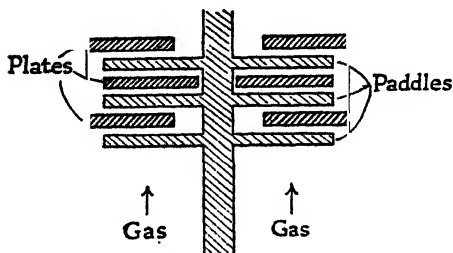
FIG. 136.   DUST-REMOVING PLANT

This temperature is too high for the catalytic reaction, so the gases are cooled to about 420°–450° by passing them through two systems of pipes air-cooled by electric fans. They next pass through mechanical filters, where dust is removed, and then enter the catalyst chambers. These chambers, of which there are usually two (in series), contain vanadium pentoxide supported on some inactive material such as asbestos. The rate of flow of the gases is so regulated that the desired temperature (420°–450°) is maintained, without application of external heat, by the exothermic reaction itself. About 80 per cent of the sulphur dioxide is converted into the trioxide in the first chamber, and the issuing gases are passed through a cooler before entering the second chamber, where the bulk of the catalyst is placed and where the remaining sulphur dioxide is oxidized.

After a further cooling, the gas mixture (SO_3, O_2, N_2) is passed up a tower down which cold 98–9 per cent sulphuric acid is sprayed; this absorbs the sulphur trioxide to form oleum. The acid leaving the absorber is diluted with water to 98–9 per cent, and sufficient of it is recirculated to the absorber. The rest is run off for storage and sale. Such a plant can be worked by a single operator, and may produce

as much as 100 tons of 98 per cent sulphuric acid daily. The average power consumption per ton of acid is 36 kilowatt-hours, which, at a cost of $\frac{1}{4}d$. per unit, is equivalent to $9d$. Oleum of various concentrations up to 25 per cent SO_3 may be obtained by absorbing the sulphur trioxide in concentrated sulphuric acid until the required concentration is reached.

Where pyrites or other sulphide-mineral is the source of the sulphur dioxide, and platinum is used as catalyst, the gases leaving the burners are passed between highly charged conductors, which cause electrostatic precipitation of solid particles (As_2O_3), etc. (LODGE-COTTRELL system). Alternatively they are washed with a spray of water, and in both cases are afterwards dried with sulphuric acid. They then pass over the catalyst at 420–450°. In some works, ferric oxide at 600–700° is employed as a preliminary catalyst; this effects oxidation of about two-thirds of the sulphur dioxide and has the advantage that no purification of the gases is necessary, since, although the efficiency of the ferric oxide is gradually impaired

FIG. 137. CONTACT TOWER

by the absorption of the impurities, it is so cheap that it can be replaced economically as often as required. The mixture of gases leaving the ferric oxide chamber is sufficiently pure for the remaining conversion to be carried out with a platinum catalyst.
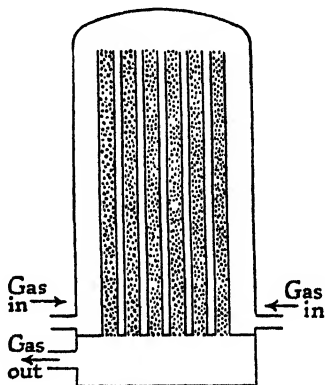
THE LEAD-CHAMBER PROCESS.—The lead chambers in which this process was formerly conducted are now obsolete, and in the more modern plants the operations are carried out in towers at a great saving of initial cost and of ground space. The sulphur dioxide, obtained by burning either pyrites or sulphur, is oxidized by air in the presence of water and oxides of nitrogen, whose action is catalytic, since only small mechanical losses have to be made up. The exact nature of the cycle of operations by which the catalyst carries out its task has long been a matter of dispute, and the problem offers peculiar difficulties because the conditions of temperature and concentration differ widely in the various parts of the reaction vessels. The suggestion that the nitrogen peroxide introduced into the system is reduced to nitric oxide and then oxidized by atmospheric oxygen in accordance with the equations:

$$SO_2+H_2O+NO_2=H_2SO_4+NO \quad \text{and} \quad 2NO+O_2=2NO_2.$$
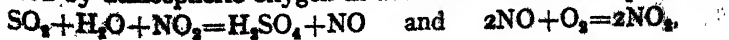
is an obvious one, but the first reaction, if attempted under conditions similar to those prevailing in the plant, will not take place. Alternative theories postulate the formation of various intermediate compounds, among them nitrosyl bisulphate $(NO)'.HSO_4'$, a compound produced in the plant when insufficient water is present, and hence known as 'chamber crystals.' Very possibly more than one of the suggested explanations is correct.

To the hot mixture of sulphur dioxide, oxygen, and nitrogen which leaves the pyrites burners, enough oxides of nitrogen (produced by the catalytic oxidation of ammonia as described on p. 390) are added to make up losses in working. The gases then pass up the Glover towers, in which in the older forms of plant they acquired
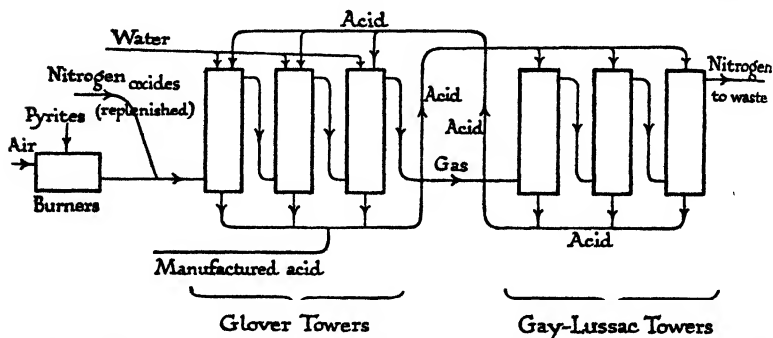
FIG. 138   SULPHURIC ACID MANUFACTURE: MODERN TOWER SYSTEM

the necessary oxides of nitrogen from a descending stream of concentrated acid. In the modern forms the sulphuric acid is actually produced in the Glover towers, of which three or more in series may be employed, and the lead chambers which gave their name to the process are dispensed with. All the towers used are filled with broken flint-stones and are lined with lead. The gases in every case pass up the tower while liquid trickles down. To the first three towers there is supplied water and acid from the last three. This acid is highly charged with oxides of nitrogen and nitric acid, and these catalyse the reaction between the incoming gases and the water in the manner already referred to. From the Glover towers the gases pass direct to the Gay-Lussac towers, in which they give up their oxides of nitrogen to acid which has passed down the Glover towers. The Gay-Lussac towers are cool, while the Glover towers, into which the hot gases pass, are hot, and this is why acid which takes up nitrogen oxides in one set can lose them in another. The finished product is withdrawn from the first

tower, where it meets hot fresh gas and is entirely freed from nitrogen compounds. It is not very concentrated, and if concentrated acid is required it must be prepared by evaporation in a ' cascade ' of basins made from fused silica, fused alumina, or other acid-resisting substances. These basins are heated from below. The contact process produces acid of any required concentration without the need of evaporation. In another process the dilute acid is sprayed into the top of another tower—the GAILLARD tower—which is supplied with an ascending current of hot producer-gas. This carries away a good deal of the water and leaves a more concentrated acid, which is collected at the bottom. Very recent forms of plant produce acid of 78 per cent concentration, which
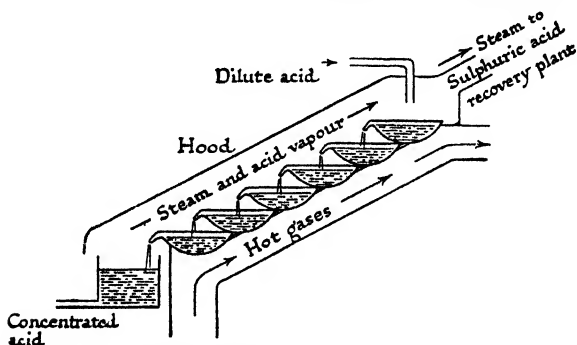
FIG. 139.   CONCENTRATING SULPHURIC ACID: CASCADE PROCESS

need not be evaporated at all. The vapours from either process contain notable quantities of sulphuric acid which is recovered as dilute acid by absorption in water. The product of the lead-chamber process or its modifications is not only less concentrated than contact acid but is also less pure, though in recent years competition has obliged the manufacturers to improve the quality by purifying the gases from the burners. The principal impurities in ' chamber ' acid are oxides of nitrogen, and arsenic, which latter may be present to the extent of 1 gm. per litre. Neither should be present in contact acid, even if made from pyrites. Nitrogen oxides can be removed by warming the acid with ammonium sulphate, which is oxidized to nitrogen and nitrous oxide:

$$2NH_4^{\cdot} + 2NO_2 = 2H^{\cdot} + N_2 \uparrow + N_2O \uparrow + 3H_2O.$$
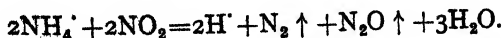
Arsenic is a very undesirable impurity and must be removed, either by heating with hydrogen chloride, when the arsenic escapes as the volatile chloride $AsCl_3$, boiling at 130°; or by precipitating the

arsenic as sulphide by treating the diluted acid with hydrogen sulphide. Other impurities which may be present in smaller quantities include hydrogen chloride, iron, selenium, aluminium, and lead.

The concentrated sulphuric acid of the laboratory contains about 96 per cent H_2SO_4, and has a density of about 1·84.

The world production of sulphuric acid is probably not far short of twelve million tons per annum, of which between one and one and a half million are produced in Great Britain. Sulphuric acid is used in almost all the chemical industries, and especially in the manufacture of fertilizers (calcium superphosphate and ammonium sulphate), which absorbs more than half the total output, sodium sulphate (for glass and salt-cake manufacture), hydrochloric and nitric acids.

Sulphuric acid, 'oil of vitriol,' 'vitriol,' H_2SO_4, manufactured in the ways described above, can be concentrated by evaporation until it contains about 98 per cent H_2SO_4. Sulphur trioxide is freely soluble in sulphuric acid, and acid called *fuming sulphuric acid, Nordhausen sulphuric acid,* or *oleum,* can be prepared with any desired content of free sulphur trioxide up to about 80 per cent of the weight of H_2SO_4. The 100 per cent acid freezes at 10°. On distillation under atmospheric pressure it loses sulphur trioxide and leaves the constant-boiling mixture with 98 per cent H_2SO_4, which boils unchanged at 330°.

Sulphuric acid is a dense, oily, highly corrosive liquid with an inordinate affinity for water, which causes it to be used for drying gases and in desiccators. From animal or vegetable tissue it removes the elements of water and leaves carbon behind, thereby becoming brown or black. If the mixture is heated, the carbon will reduce some of it to sulphur dioxide. The great heat developed when sulphuric acid and water are mixed may lead to dangerous explosions; it is much safer to add the acid to the water than the water to the acid. The study of the freezing-points of sulphuric acid-water systems indicates the existence of hydrates, $H_2SO_4.H_2O$, $H_2SO_4.2H_2O$, and $H_2SO_4.4H_2O$, and others may exist in solution. The vapour obtained by boiling the acid is largely dissociated into sulphur trioxide and water:

$$H_2SO_4 \rightleftharpoons H_2O + SO_3,$$
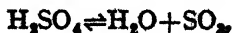
and this dissociation is increased by raising the temperature or reducing the pressure.

The constitution of sulphuric acid is very probably

$$\begin{array}{c} H-O \\ H-O \end{array} \Big\rangle S \Big\langle \begin{array}{c} O \\ O \end{array}$$
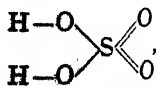
and this formula agrees very well with its chemical behaviour. Apart from the decomposition into sulphur trioxide and water on

heating, it may in its reactions decompose in three ways according to the conditions:

1. As an acid: $H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4'$ followed by $HSO_4' \rightleftharpoons H^{\cdot} + SO_4''$.
2. As an oxidizing agent: $H_2SO_4 \rightarrow H_2O + SO_2 + O$.
3. As a sulphonating agent: $2H_2SO_4 \rightleftharpoons HSO_3' + HSO_4' + H_2O$.

1. The *acid decomposition* takes place only when the hydrogen ions can be removed from the system or can enter into combination. Water promotes the ionization of all acids by forming hydrated hydrogen ions:

$$H_2SO_4 + 2nH_2O \rightleftharpoons 2(H.nH_2O)^{\cdot} + SO_4'',$$
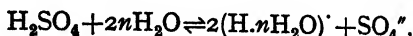
and in aqueous solution sulphuric acid is a strong acid, at any rate in its first dissociation. The dissociation-constant of its second dissociation, $HSO_4' \rightleftharpoons H^{\cdot} + SO_4''$, is about 0·03, so that sulphuric acid is not quite so strong as the typical strong acids. In careful potentiometric titration a faint point of inflection can be detected corresponding with HSO_4', but this does not affect the titration of sulphuric acid solutions with indicators. Suitable metals will displace hydrogen from dilute sulphuric acid in the ordinary way.

The acid decomposition can also take place when the concentrated acid is heated with the salts of more volatile acids:

$$H^{\cdot} + Cl' \rightarrow HCl \uparrow.$$
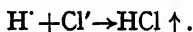
The high boiling-point of sulphuric acid is responsible for its well-known power of expelling acids from their salts, since the maximum possible concentration of (e.g.) hydrogen chloride in the liquid phase at high temperatures is very small.

2. The hot acid acts as an *oxidizing agent* if water is absent and suitable reducing agents are present. Metals usually liberate sulphur dioxide from the hot concentrated acid, and they may further reduce it to hydrogen sulphide, while sulphur is often formed from the sulphur dioxide and hydrogen sulphide. A high temperature, which reduces the maximum possible concentration of sulphur dioxide, is usually required for these reactions. BOYLE discovered that sulphuric acid could be partially reduced to sulphur by distillation with turpentine.

3. At low temperatures and in the presence of substances containing hydrogen, but in the absence of water, sulphuric acid acts as a *sulphonating agent*:

$$\underset{\text{benzene}}{C_6H_6} + H_2SO_4 = \underset{\substack{\text{benzene} \\ \text{sulphonic acid}}}{C_6H_5.SO_3H} + H_2O.$$
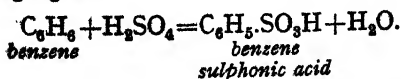
The real agent is the cation $HSO_3^{\cdot}$ ($RH + HSO_3^{\cdot} = RHSO_3^{\cdot} + H^{\cdot}$), which, as equation 3 shows, is formed freely only in the absence of

water, hence the reaction is assisted by the use of fuming sulphuric acid, which contains free sulphur trioxide. If the system is allowed to get too hot the product may be oxidized and the sulphuric acid reduced.

Sulphuric acid was formerly used for removing the elements of water from other substances, e.g. with its help alcohol can be converted to either ether or ethylene:

$$2C_2H_5.OH - H_2O = (C_2H_5)_2O. \qquad C_2H_5.OH - H_2O = C_2H_4$$
$$\textit{alcohol} \qquad\qquad \textit{ether} \qquad\qquad \textit{alcohol} \qquad\qquad \textit{ethylene}$$
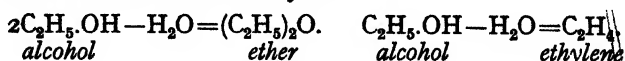
Sulphates.—These are described under the metals. The sulphates of (radium), barium, strontium, calcium, silver, lead, and mercury (-ous) are insoluble or only slightly soluble in water. The acid sulphates or bisulphates such as $NaHSO_4$ all lose sulphuric acid on strong heating, yielding the normal sulphate:

$$2NaHSO_4 = Na_2SO_4 + H_2SO_4 \uparrow .$$

Chlorsulphonic acid, $ClSO_3H$, is the acid monochloride of sulphuric

acid and has the formula $\overset{\displaystyle Cl}{\underset{\displaystyle H-O}{\diagdown}}S\overset{\displaystyle O}{\underset{\displaystyle O}{\diagup}}$. It can be prepared by

the combination of hydrogen chloride and sulphur trioxide:

$$HCl + SO_3 = Cl.SO_3H,$$
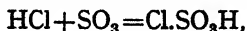
or more conveniently by passing hydrogen chloride into fuming sulphuric acid (which contains free sulphur trioxide) at room temperature. The chlorsulphonic acid is then distilled off and purified by distillation. It is a colourless, dense, fuming liquid, boiling at 155°, which reacts violently with water, forming hydrogen chloride and sulphuric acid, and is used in organic chemistry to produce sulphochlorides:

$$RH + Cl.SO_3H = R.SO_2Cl + H_2O.$$
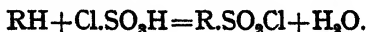
Sulphur sesquioxide, S_2O_3.—This is a blue substance obtained by adding sulphur to molten sulphur trioxide at 15°. It is unstable and readily decomposes into sulphur and sulphur dioxide:

$$2S_2O_3 = S + 3SO_2 \uparrow ,$$

and is immediately decomposed by water, forming a mixture of acids.

Dithionous acid, $H_2S_2O_4$.—It should be noticed that this acid is not produced when sulphur sesquioxide is treated with water. *Sodium dithionite,* $Na_2S_2O_4$, is produced on the large scale by reducing a solution of sodium hydrogen sulphite with zinc:

$$2HSO_3' + Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + S_2O_4'' + 2H_2O.$$
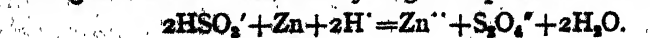
If the liquid is kept cold, most of the dissolved zinc is removed as an insoluble double sulphite. The hydrate $Na_2S_2O_4.2H_2O$ can be obtained from the solution, and must be dehydrated (as it is unstable) by washing with alcohol. The product is used in the dyeing industry as a reducing agent.

A solution of dithionous acid can be prepared by acidifying a solution of sodium dithionite, or by electrolytic reduction of sulphurous acid, but the free acid is very unstable even in solution, and has not been isolated. Its solutions, which have a repulsive smell, are very powerful reducing agents. The acid is nearly as strong as sulphuric acid.

Thiosulphuric acid, $H_2S_2O_3$.—The manufacture of sodium thiosulphate, $Na_2S_2O_3.5H_2O$, from alkali-waste has already been described (p. 452). Solutions of this substance can also be prepared by boiling sodium sulphite solutions with sulphur:

$$SO_3'' + S = S_2O_3''.$$

Its solutions are used in photography as solvents for silver halides, which dissolve in them with the formation of a complex silver thiosulphate ion:

$$AgBr \downarrow + S_2O_3'' \rightleftharpoons AgS_2O_3' + Br',$$
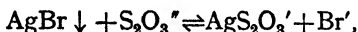
a reaction very similar to that between sulphites and silver salts (p. 472). Sodium thiosulphate is very widely used in the laboratory as a volumetric reagent for the estimation of iodine (usually dissolved in solutions of potassium iodide), by which it is converted to a tetrathionate:

$$I_2 + 2S_2O_3'' = 2I' + S_4O_6''.$$
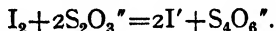
With chlorine or bromine, on the other hand, a sulphate is produced:

$$4Cl_2 + S_2O_3'' + 5H_2O = 8Cl' + 2SO_4'' + 10H^{\cdot},$$
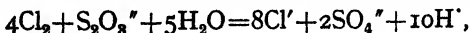
but these reactions are much less suitable for volumetric analysis. Sodium thiosulphate, like sodium sulphite, is used as an antichlor. Its solutions are fairly stable in air, though on long standing they may deposit a little sulphur; consequently the concentration of such solutions must be fairly frequently checked when they are used for volumetric analysis.

The thiosulphates can be oxidized without difficulty either to tetrathionates or sulphates. When treated with acids they evolve sulphur dioxide, just as sulphites do, but they can be distinguished from sulphites by the sulphur which they deposit at the same time:

$$S_2O_3'' + 2H^{\cdot} = SO_2 \uparrow + S \downarrow + H_2O.$$

POLYTHIONIC ACIDS.—These acids or their salts may be prepared by special methods, some of which are briefly epitomized in the

following equations of reactions in aqueous solution, at room temperature, unless otherwise indicated.

(1) *Dithionate:*
$$2Na_2SO_3+2AgNO_3=Na_2S_2O_6+2NaNO_3+2Ag \downarrow \ (100°).$$

(2) *Trithionate:*
$$Na_2S_2O_3+2NaHSO_3+2SO_2=2Na_2S_3O_6+H_2O.$$

(3) *Tetrathionic acid:*
$$S_2Cl_2+2SO_2+2H_2O=H_2S_4O_6+2HCl.$$
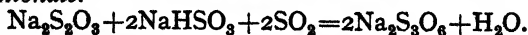
(4) *Pentathionic acid:*
$$5Na_2S_2O_3+10HCl=2H_2S_5O_6+3H_2O+10NaCl \ (-10°).$$
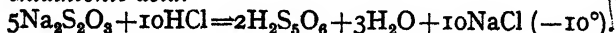
The polythionic anions may be written $O=S \underset{O^-}{\overset{O}{\diagup}} S_n \diagdown \underset{O^-}{\overset{O}{\diagdown}} S=O$, in which

n runs from o to probably 4. The n sulphur atoms link the (SO_3)-groups in a simple chain.

Sulphur heptoxide, Persulphuric anhydride, S_2O_7, is made by exposing a mixture of sulphur dioxide or sulphur trioxide and oxygen to the silent discharge.
$$4SO_3+O_2=2S_2O_7.$$
Sulphur heptoxide is a colourless liquid freezing at o°, which, on warming, readily decomposes into sulphur trioxide and oxygen. It dissolves in water with the evolution of much heat to give a solution of persulphuric acid, $H_2S_2O_8$, called perdisulphuric acid to distinguish it from permonosulphuric acid, H_2SO_5.
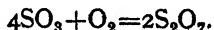
Persulphuric acid, $H_2S_2O_8$.—This acid has the structure
$$HSO_3—O—O—HSO_3.$$
It can be synthesized by the action of hydrogen peroxide on chlorsulphonic acid:
$$SO_2.OH.Cl+H.O.O.H+Cl.OH.SO_2=SO_2.OH.O.O.OH.SO_2+2HCl.$$
The most convenient method of preparing a solution of this substance is the electrolysis of not too concentrated sulphuric acid (40 per cent) in a diaphragm cell at a low temperature with a small smooth platinum anode and a high current density. Under these conditions the oxygen over-voltage is a maximum.
$$2HSO_4'=H_2S_2O_8+2 \ electrons.$$
By using anhydrous hydrogen peroxide and chlorsulphonic acid, as described above, the anhydrous acid can be prepared. It is a fairly stable solid, melting at 65°, which readily loses oxygen on warming and is a powerful oxidizing agent.
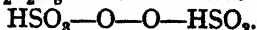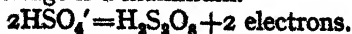
Sulphur tetroxide, SO_4, is a white solid, M.P. 3°, obtained when a mixture of sulphur dioxide with excess of oxygen is subjected to the glow electric discharge at low pressure (less than 1 mm.). It is

a powerful oxidizing agent, converting manganous salts into permanganates and aniline into nitrobenzene. From its formula it would appear to be the anhydride of *permonosulphuric acid*, H_2SO_5, but this acid is not formed when the tetroxide is dissolved in water.

Permonosulphuric acid, H_2SO_5, sometimes called **Caro's acid,** after its discoverer, is prepared by the anodic oxidation of *concentrated* sulphuric acid, or by treating potassium perdisulphate with concentrated sulphuric acid, a curious reaction which is apparently a hydrolysis:

$$HO_3S.O.O.SO_3H + H_2O = HO_3S.O.OH + H_2SO_4.$$
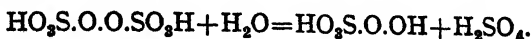
The anhydrous acid may be prepared from hydrogen peroxide and half the amount of chlorsulphonic acid required for the conversion to perdisulphuric acid:

$$HO_3S.Cl + H.O.O.H = HO_3S.O.OH + HCl,$$
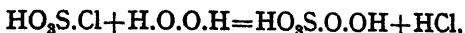
and this shows the acid to be a sulphonation product of hydrogen peroxide. The anhydrous acid melts at $45°$. It is a powerful oxidizing agent resembling perdisulphuric acid in its behaviour, but its active oxygen, as might be expected from the constitutional formulae of the two compounds, is more easily accessible. Solutions of permonosulphuric acid, like solutions of hydrogen peroxide, will liberate iodine fairly rapidly from iodide solutions, whereas with perdisulphuric acid the action is much slower.

The persulphates are produced on the manufacturing scale by electrolysis for use in the dyeing industry as oxidizing agents, and for the preparation of hydrogen peroxide.

THE HALIDES OF SULPHUR.—Sulphur combines with all the halogens except iodine to form halides, which are volatile substances decomposed by water, with the exception of sulphur hexafluoride, the stablest member of the series, and a compound in which sulphur displays its maximum covalency.

Fluorides.—Sulphur burns in fluorine, the principal product being *sulphur hexafloride*, SF_6, a colourless gas, boiling-point $-64°$, melting-point $-51°$. It is a very stable inert substance, unchanged on heating, nearly insoluble in water, and unaffected by fused caustic potash. It can, however, be decomposed by strong reducing agents such as boiling sodium, or by sparking with hydrogen.

Sulphur decafluoride, S_2F_{10}, a liquid boiling at $29°$, is produced with the hexafluoride when sulphur burns in fluorine, and is as unreactive as the latter. The constitution is F_5S-SF_5.

Sulphur monofluoride, S_2F_2, is probably obtained when sulphur is heated with silver fluoride.

Chlorides.—Sulphur reacts with chlorine at the ordinary temperature, the first product being *sulphur monochloride*, S_2Cl_2, the

most stable chloride of sulphur. The product of the reaction is purified by distillation at 138°, which frees it on the one hand from the less volatile sulphur, and on the other from the more volatile sulphur dichloride. The monochloride is a fuming yellow liquid with a suffocating odour; it is decomposed by water, with the formation of hydrochloric acid, sulphur, and a mixture of sulphur oxyacids, and on heating is partially decomposed into sulphur dichloride and sulphur:

$$S_2Cl_2 \rightleftharpoons SCl_2 + S.$$
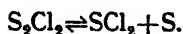
It is used in the chlorination of organic compounds, and also in the preparation of inorganic chlorides. Electron diffraction shows S_2Cl_2 to have the structure $\overset{Cl}{\diagdown}_{S-S}\overset{Cl}{\diagup}$. When sulphur is exposed for a longer period to the action of chlorine in excess, *sulphur dichloride*, SCl_2, is obtained, and can be purified by distillation at 50° in a rapid current of chlorine. It is a heavy brown liquid, fuming in air, and with a strong smell resembling that of chlorine: its reaction with water is similar to that of the monochloride. It gives off chlorine slowly at ordinary temperatures and more rapidly on heating, leaving the monochloride. *Sulphur tetrachloride*, SCl_4, is a yellow solid which can exist only at low temperatures, say below —30°; on melting it decomposes into the dichloride and chlorine. It is prepared by the action of chlorine on the monochloride at a low temperature.

Bromides.—Sulphur and bromine probably form only one compound, *sulphur monobromide*, S_2Br_2, easily obtained by heating the elements together in a sealed tube on the water-bath. It is a heavy red liquid, freezing at —40° and fuming in air. It is decomposed by water and is also decomposed into its elements on heating.

OXYHALIDES OF SULPHUR.—Sulphur forms two principal series of oxyhalides: the sulphuryl halides, such as SO_2Cl_2, the acid dichloride of sulphuric acid, and the thionyl halides, such as $SOCl_2$, the acid dichloride of sulphurous acid.

Sulphuryl fluoride, SO_2F_2, is prepared by combination from sulphur dioxide and fluorine. Like sulphur hexafluoride, it is a very stable colourless gas, only slightly soluble in water.

Sulphuryl chloride, SO_2Cl_2, can be obtained by combination from sulphur dioxide and chlorine. The action takes place slowly in sunlight and can be accelerated by a catalyst, such as charcoal or camphor. It can also be prepared without difficulty by boiling the acid monochloride—chlorsulphonic acid—with a little mercuric sulphate as catalyst:

$$2Cl.SO_2H = H_2SO_4 + SO_2Cl_2 \uparrow.$$

Sulphuryl chloride is the most volatile constituent of the resulting

mixture, and can be distilled off through a reflux condenser at 70°, which retains the chlorsulphonic acid. It is a colourless liquid, fuming in air, and with a suffocating smell; it boils at 70°, but the vapour is partially dissociated. When mixed with water it evolves much heat, and forms first chlorsulphonic acid, then hydrochloric and sulphuric acids:

$$SO_2Cl_2 + H_2O = Cl.SO_3H + HCl. \qquad Cl.SO_3H + H_2O = H_2SO_4 + HCl.$$

Thionyl chloride, $SOCl_2$.—Numerous methods are available for the preparation of this compound. It may be obtained by the action of phosphorus pentachloride on sulphur dioxide or the sulphites:

$$SO_2 + PCl_5 = SOCl_2 + POCl_3,$$
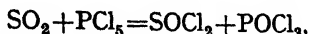
or by heating sulphur trioxide with sulphur monochloride:

$$SO_3 + S_2Cl_2 = SOCl_2 \uparrow + SO_2 \uparrow + S.$$

It is a heavy colourless liquid with a strong smell, and boils at 78°; it can readily be distilled without decomposition if water-vapour is excluded. It is immediately decomposed by water, forming hydrochloric acid and sulphur dioxide:

$$SOCl_2 + H_2O = SO_2 \uparrow + 2HCl.$$

Thionyl chloride is used in organic chemistry to replace hydroxyl by chlorine:

$$2ROH + SOCl_2 = 2RCl + H_2O + SO_2.$$
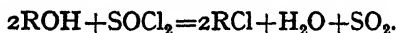
Thionyl fluoride, SOF_2, and **thionyl bromide,** $SOBr_2$, have also been prepared, but thionyl iodide is unknown.

Sulphur nitrides and **sulphur phosphides.**—See pp. 425 and 636.

SELENIUM

$Se = 78 \cdot 96$. *Atomic Number*, 34

History.—It is possible that ARNOLD OF VILLANOVA (early fourteenth century?) was the first to notice selenium, since he mentions a ' red sulphur ' attached to the walls of a chamber in which crude sulphur had been vaporized. The effective discovery of the element was, however, made in 1817 by BERZELIUS, who isolated it from the red powder that had collected on the floors of a sulphuric acid works. He found that it closely resembled tellurium (q.v.), and was therefore induced to call it *selenium*, from the Greek σελήνη, the moon, since tellurium had been named from *tellus*, the earth.

Occurrence and Extraction.—Selenium is one of the rarer elements, and occurs only in small quantities in ores, usually as the selenide of

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a metal. The selenium of commerce is therefore extracted from the deposit which collects during the manufacture of sulphuric acid. There are several methods of extracting the selenium from this deposit. One of the best is to heat the dried deposit in a stream of chlorine, when the volatile chlorides of sulphur and selenium are driven off and may be retained in water. The resulting liquid is then filtered and made very strongly acid with hydrogen chloride. The selenium can then be precipitated in the elementary state with sulphur dioxide, leaving all the sulphur and tellurium (if any is present) in solution; though if the solution is not sufficiently acid the tellurium will come down as well. It may be purified by dissolving it in hot concentrated sulphuric acid, which converts it to the dioxide SeO_2, and pre-

cipitating the diluted solution with sulphur dioxide.

Properties.—Selenium occurs in three principal allotropic forms, whose relations can be followed from the diagram.
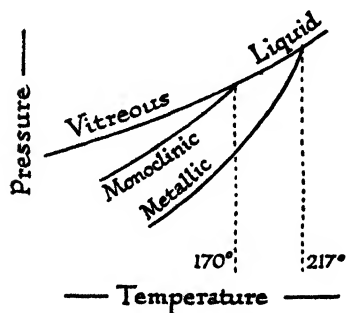
FIG. 140. THE ALLOTROPY OF
SELENIUM

1. The vitreous or *amorphous* form is an undercooled liquid which is precipitated from selenium solutions by reduction, as for instance with sulphur dioxide. Colloidal selenium belongs to this variety, which, like certain forms of sulphur, is soluble in carbon disulphide.

2. A *monoclinic* variety, also soluble in carbon disulphide, is deposited from hot solutions of selenium as small red crystals. These melt in the neighbourhood of 170°, if rapidly heated, but at this temperature all forms of the element pass fairly soon into the metallic form.

3. *Metallic* selenium has the lowest vapour pressure and is consequently the most stable; all other forms revert to it with a velocity which can be accelerated by heating. It is a grey crystalline substance, density 4·8, isomorphous with tellurium and insoluble in carbon disulphide. It melts at 217°. This form of the element has some metallic characteristics, and among them the power of conducting electricity, which though feeble is readily distinguishable from the insulating power of such a substance as sulphur. It was noticed by W. SMITH in 1873 that the resistance of selenium was very markedly affected by illuminating the element. When selenium is exposed to light the resistance falls, rapidly at first, and then more slowly until a constant and much lower value is reached.

On removing the illumination the original resistance is recovered rather more slowly than it was lost.

The change in resistance cannot be attributed to a change in temperature, for the same effect is noticeable if the selenium is kept under water during exposure. It is supposed that light stimulates the expulsion from selenium atoms of the free electrons to which electrical conductivity is due, and provides the necessary energy; then, in the dark the free electrons, or some proportion of them, recombine with positive ions. An alternative but not necessarily exclusive theory postulates a new allotropic form of selenium, of lower specific resistance, produced by the influence of light. Whatever the explanation, this property of selenium has been put to practical use in photoelectric cells, in which a short thin plate of selenium is connected with a relay. Such an apparatus can be made to ring an alarm when exposed to the lantern of a burglar, or to start a lighthouse at dusk and extinguish it at dawn. In recent years such
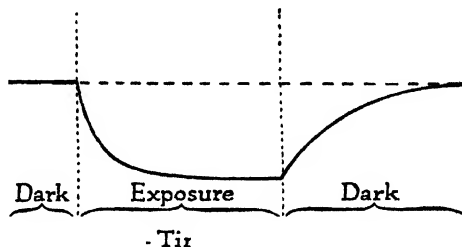
FIG 141. EFFECT OF EXPOSING SELENIUM TO LIGHT

cells have also been used in certain forms of sound films and of television, and in a new type of gramophone in which the record consists of a perforated paper strip.

Selenium is stable in the air, but burns on strong heating, forming, as does sulphur, the dioxide with a little of the trioxide. Like sulphur, selenium can be made to combine with almost all elements. It is unaffected by hydrogen ions, but is easily oxidized and will dissolve in dilute nitric acid as the dioxide, SeO_2, or perhaps as selenious acid, H_2SeO_3.

When selenium vapour is heated the complexity of the molecules, as determined by vapour-density measurements, is gradually reduced from about Se_6 at about $200°$ to Se_2, and at, say, $1400°$ the change is nearly complete.

Hydrogen selenide, H_2Se, made by the union of the elements at $500°$ or by the action of water on aluminium selenide, is a colourless poisonous gas with an odour recalling that of hydrogen sulphide. It is much less stable than this compound, as is shown by its reaction with sulphur:

$$H_2Se + S = H_2S + Se,$$
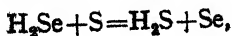
and is slowly but completely decomposed into its elements at ordinary temperatures if exposed to sunlight. By moist air it is fairly rapidly decomposed into selenium and water:

$$2H_2Se+O_2=2Se+2H_2O,$$
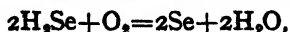
and in its behaviour on burning it resembles hydrogen sulphide. It is fairly soluble in water, but the solution deposits selenium if exposed to the air. With solutions of the salts of most metals hydrogen selenide precipitates insoluble selenides, but the selenides of the alkali-metals are soluble in water. In these solutions hydrogen selenide, a very feeble acid, is formed by hydrolysis, and unless they are isolated from the air they deposit selenium.

Selenium dioxide, SeO_2, is prepared by burning selenium (a high temperature is required), or by evaporating to dryness nitric acid in which selenium has been dissolved. It is a colourless solid with yellowish-green vapour; it sublimes on heating and the vapour pressure reaches 760 mm. at 315°. It is much less stable than sulphur dioxide and will readily part with its oxygen: it will, for example, oxidize ammonia gas to nitrogen:

$$3SeO_2+4NH_3=2N_2+3Se+6H_2O.$$
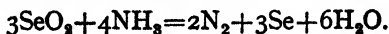
In solution, however, it has feeble reducing properties. It is very soluble in water, and by cautious evaporation of the solution **selenious acid,** H_2SeO_3, can be prepared, a stable substance also produced when the dioxide is exposed to moist air. Selenious acid is rather weaker than sulphurous acid. Selenite solutions, which contain the ion SeO_3'', are much feebler reducing agents than the sulphites. They can be completely oxidized by chlorine but not by iodine, while with bromine an equilibrium is reached (N.B.— Sulphites will reduce all the halogens):

$$SeO_3''+H_2O+Br_2 \rightleftharpoons SeO_4''+2H^{\cdot}+2Br'.$$
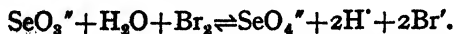
On the other hand concentrated selenic acid will oxidize hydrochloric acid to chlorine, so the reaction is really a reversible one. The reactions with the analogous sulphur compounds are interesting. Selenium is deposited from selenium dioxide or selenious acid by reduction with either sulphur, hydrogen sulphide, or sulphur dioxide:

$$SeO_2+S=Se \downarrow +SO_2.$$
$$H_2SeO_3+2H_2S=Se \downarrow +2S \downarrow +3H_2O.$$
$$H_2SeO_3+2SO_2+H_2O=Se \downarrow +2H_2SO_4.$$
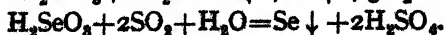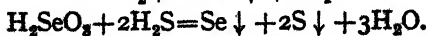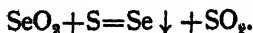
Selenium trioxide, SeO_3, has, with difficulty, been prepared as a white sublimate, by passing a glow discharge through oxygen in the presence of selenium.

It is a pale yellow solid which reacts with water to form selenic acid, and when heated to 120° yields the dioxide and oxygen.

Selenic acid, H_2SeO_4.—Selenates such as K_2SeO_4 can be prepared by fusing selenium or a selenite with the nitrate of an alkali-metal, or by oxidizing a selenite solution either with chlorine or electrolytically. By acidifying selenate solutions and concentrating them, it is possible to prepare crystals of anhydrous selenic acid. These crystals melt at 61° and, like sulphuric acid, develop much heat when mixed with water. Selenic acid is a far stronger oxidizing agent than sulphuric acid, and begins to decompose into selenium dioxide and oxygen at about 200°. In its action on organic substances it resembles sulphuric acid, but it will oxidize hydrogen chloride to chlorine and, if hot and concentrated, will also dissolve gold, being thereby reduced to selenious acid. More energetic reducing agents, such as sulphur dioxide, reduce it to selenium. The selenates in other respects somewhat resemble the sulphates, and there is a striking similarity between the solubility curves of sodium selenate and sodium sulphate (p. 130), the transition-temperatures being nearly identical. Barium selenate is insoluble in water, but may be distinguished from barium sulphate by the power, which it shares with the soluble selenates, of oxidizing hydrochloric acid.

Halides.—These compounds resemble the halides of sulphur, though there are important differences, e.g. no dichloride is known. *Selenium hexafluoride*, SeF_6, like sulphur hexafluoride, is a stable gas, quite unaffected by water, the covalency maximum of both elements being six; compare the chlorides of carbon and silicon. *Selenium tetrafluoride*, SeF_4, is made from selenium tetrachloride and silver fluoride. It is a colourless fuming liquid, melting-point −13°, boiling-point 93°.

Selenium tetrachloride, $SeCl_4$, prepared by union of the elements, is at ordinary temperatures a solid substance which sublimes on heating. The vapour pressure reaches 760 mm. at 196°.

TELLURIUM

Te=127·61. *Atomic Number,* 52

History.—In 1782 VON REICHENSTEIN suspected that the Transylvanian mineral known as white gold ore (*Weissgolderz*), generally supposed to be an alloy of antimony and bismuth, in reality contained a hitherto unknown element. This suspicion was confirmed by BERGMANN, and before the end of the eighteenth century

KLAPROTH had isolated the element and investigated its principal properties. The name is derived from *tellus*, the earth.

Occurrence and Extraction.—Tellurium is a comparatively rare element which occurs in small quantities in many parts of the world, among them Rumania, Brazil, and the United States. The most important ore is perhaps bismuth telluride, Bi_2Te_3, and tellurium is extracted from the alkaline residues of bismuth ores (p. 656). These are dissolved in hydrochloric acid and the tellurium is precipitated in the elementary state by sulphur dioxide, but tellurium, which is more metallic in its behaviour than selenium, cannot be precipitated from very strongly acid solutions. The pure element may be obtained:

(i) By reducing the dioxide with hydrogen and distilling the product in hydrogen under reduced pressure.
(ii) By electrolysis of a solution prepared from the dioxide and concentrated hydrofluoric acid, with a little sulphuric acid.

Properties.—Tellurium is a silver-white substance of metallic appearance, with a fairly high melting-point (452°). It is very brittle, and is usually supplied in powder form. By precipitation from aqueous solutions a brown amorphous variety is obtained. This is insoluble in all solvents except those with which it reacts, and is converted to the crystalline or metallic variety on heating. The vapour appears to be diatomic at all temperatures. Pure tellurium probably does not conduct electricity.

Tellurium is unaffected by hydrogen ions, but will dissolve in oxidizing acids, while caustic potash dissolves it, forming a telluride and a tellurite (compare sulphur):

$$3Te+6OH'=2Te''+TeO_3''+3H_2O.$$
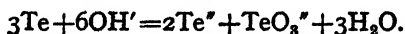
Hydrogen telluride, H_2Te, is prepared (i) by the action of dilute acids on aluminium telluride, Al_2Te_3, itself obtained by union of the elements; or (ii) by electrolysing dilute sulphuric acid with a tellurium cathode. It boils at 2° and is a highly unstable gas, decomposing spontaneously even in the dark and rapidly decomposed by air into tellurium and water. In odour it somewhat resembles hydrogen sulphide and selenide.

The tellurides resemble the selenides, but the soluble tellurides—i.e. those of the alkali-metals—are even less stable in solution than the soluble selenides and are very readily oxidized with the precipitation of tellurium.

Tellurium dioxide, TeO_2, is formed when tellurium burns in the air, and can also be prepared by dissolving tellurium in warm dilute nitric acid and evaporating to dryness. It is a white solid

which differs from selenium dioxide in being insoluble in water. It will, however, dissolve in acids, and is in fact amphoteric, though its basic properties are excessively weak. The salts of tellurium are all decomposed by water and can exist only in strongly acid solution. **Tellurium sulphate,** $Te(SO_4)_2$, can, however, be isolated as a colourless crystalline solid from its solutions in concentrated sulphuric acid.

Tellurous acid, H_2TeO_3, cannot be prepared by the action of water on the dioxide, but is precipitated when the nitric acid solution is poured into water, in which it is not very soluble. The tellurites, like the tellurates, usually have more complex constitutions than the simple formula suggests. They are readily reduced to tellurium or oxidized to tellurates, as for instance by permanganates.

Telluric acid, H_6TeO_6.—This compound can be prepared by methods similar to those used for the preparation of selenic acid, but it differs in constitution from selenic or sulphuric acids. If the tellurates are formulated as though they were derived from H_2TeO_4, it is found that they retain two molecules of water of crystallization per molecule of salt which cannot be removed without decomposing them. The formula of such a compound as $BaTeO_4.2H_2O$ should therefore be written $BaH_4(TeO_6)$, and this view is supported by the existence of organic compounds such as $Te(OCH_3)_6$ and of salts such as $Ag_6(TeO_6)$. In Group VII the adjacent element iodine shows a very similar behaviour.

Like the selenates, the tellurates are oxidizing agents which will liberate chlorine from hydrogen chloride. Telluric acid is very soluble in water: on heating it yields first **tellurium trioxide,** TeO_3, then the dioxide and oxygen.

HALIDES.—The halides of tellurium, though largely covalent, yet show traces of salt-like character, and the tetrahalides can exist in solution if sufficient acid is present to prevent hydrolysis. They are usually prepared by union of the elements. The **hexafluoride,** TeF_6, is decomposed by water. The tetrahalides are more stable than those of selenium, and much more stable than those of sulphur: the **tetrachloride** is a colourless crystalline substance which melts at 225° and can be boiled without decomposition at 390°. The molten salt has a fairly high electrical conductivity. The **tetraiodide** is unaffected by cold water, in which it does not dissolve, though it is decomposed on boiling.

SUBGROUP A

CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

	Cr	Mo	W	U
Atomic Number	24	42	74	92
Atomic Weight	52·01	95·95	183·86	238·07
Density	6·9	9·1	18·7	18·7
Atomic Volume	7·6	10·6	9·9	12·7
Melting-point	1900°	2620°	3370°	1150°

These elements are all dense, silvery-white, rather hard metals with small atomic volumes and high melting-points. In their compounds the transitional character, as denoted by variable valency and by colour, is very marked; chromium, for instance, is part of the series of elements V, Cr, Mn, Fe, Co, Ni in which these properties are apparent, and the same applies to the other elements of the subgroup. The relationship between the transition elements is discussed on p. 771. In addition to the group valency of six, well-defined valencies of two, three, four, and five may occur, and this makes the chemistry of the elements in this subgroup a complicated study. These valencies may be considered in order:

Two.—The bivalent compounds are all powerful reducing agents, as might be expected. They are all salts showing a tendency to associate.

Three.—Chromium forms a stable and important series of compounds in which it is tervalent, but with the other elements the tervalent compounds are of less importance. The stability of the tervalent chromium compounds is probably due to the facility with which chromium forms complex ions, even in aqueous solutions, in which its electrovalency is three and its co-ordination number six. The hydrated sesquioxide of chromium is a weak base, so the salts are hydrolysed, and is alone in displaying weak acidic properties and in forming compounds with bases—the chromites.

Four.—Only tungsten and uranium form quadrivalent salts stable in solution: they are reducing agents easily converted to the sexivalent state.

Five.—It is probable that chromium can be quinquevalent, and quinquevalent compounds of molybdenum are well established.

Six.—This is the group valency, and is conspicuous in all the elements of this subgroup: the sexivalent compounds are almost the only links with Subgroup B. Such are the hexafluorides, formed by all the elements except chromium; they are all covalent compounds decomposed by water. All the elements form acidic

trioxides whose acidity diminishes with increasing atomic number; uranium trioxide is amphoteric. By dissolving these trioxides in water, acids of formula such as H_2MO_4 are obtained, but they all show a tendency, noticeable even in chromium, to form condensed acids of higher molecular weight. The simple salts are often isomorphous with the sulphates and selenates.

The stability of the higher valencies increases with the atomic number. The oxidizing powers of chromic acid are due to the pre-ference of chromium for the tervalent state, and are faintly repro-duced in molybdic acid but absent elsewhere. Thus the ignition of ammonium dichromate yields the sesquioxide, but the ignition of ammonium diuranate the trioxide. All the elements form coloured peracids of uncertain constitution.

Of the individual elements, chromium is by far the most abundant. Molybdenum and tungsten, like the preceding pairs of elements zirconium and hafnium, niobium and tantalum, closely resemble each other. The complexity of their valency relations and their very marked tendency to form condensed compounds make their chemistry difficult. Uranium is distinguished by its radioactive properties, by the stability of its quadrivalent compounds, and by the series of uranyl salts produced by dissolving the amphoteric trioxide in acids.

CHROMIUM

Cr=52·01. *Atomic Number*, 24

History.—In 1762-6 LEHMANN described a new mineral called *crocoite* or *crocoisite*. In 1797, VAUQUELIN showed that it consisted of oxide of lead combined with the oxide of a new metal which he proposed to call *chromium*, on account of its characteristic property of forming coloured compounds (Greek χρῶμα, colour). He was able to isolate the metal in an impure state by the fusion of chromic acid with carbon. Purer specimens were made by DEVILLE in 1857, but it was not till 1894 that the reasonably pure element was prepared, by MOISSAN.

Occurrence and Extraction.—Chromium is a fairly abundant element which occurs principally as *chromite*, Cr_2O_3,FeO, sometimes called *chrome iron ore*, which is found in South Africa, Russia, the United States, India, and elsewhere. This mineral is washed, finely ground with lime and potassium carbonate, and roasted. Potassium chromate is thereby produced:

$$4K_2CO_3 + 2Cr_2O_3 + 3O_2 = 4K_2CrO_4 + 4CO_2 \uparrow.$$
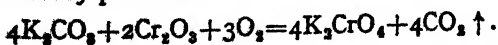
This is a soluble substance which is extracted by water and converted

*z

to potassium dichromate, $K_2Cr_2O_7$, by adding sulphuric acid and recrystallizing:

$$2CrO_4'' + 2H' = Cr_2O_7'' + H_2O.$$
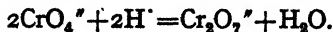
The potassium dichromate is then reduced to a chromite, $K_2Cr_2O_4$, by heating with starch or some other reducing agent, and chromium sesquioxide in a more or less pure state is obtained from this by washing, since all soluble chromites are decomposed by water:

$$K_2Cr_2O_4 + H_2O = Cr_2O_3 + 2KOH.$$
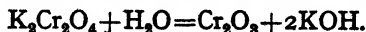
This chromium sesquioxide is the source of the metallic chromium of commerce. Its reduction to the metal can be effected by the usual powerful reducing agents, such as carbon or the alkali-metals, but only with difficulty, and on the commercial scale of the GOLD-SCHMIDT process (p. 533) is used, one or two hundredweights of the metal being produced from each charge. Since, however, a large proportion of the chromium used in industry is for the purpose of plating, it is simpler to dissolve the dichromate in sulphuric acid and plate direct from this solution.

Properties.—Chromium is a hard white or greyish metal. It melts at 1900° and boils at about 2470°. It is extremely stable in the air, and to this is due its extensive use as a plating metal. It must be heated to some 2000° before it will combine with oxygen; the product is then the sesquioxide. The standard electrode potential (with respect to chromic solutions) is about −0·7 volt, but the metal will not dissolve in water, perhaps on account of the formation of a film of oxide, and chromium plating is possible if the conditions are carefully controlled. It dissolves fairly readily in acids on warming, forming, if air is excluded, solutions of chromous salts, but in oxidizing solutions such as concentrated nitric acid it rapidly becomes passive (p. 423). It will, however, reduce hot concentrated sulphuric acid to sulphur dioxide.

Chromium is added to steel to make it hard and tough, and alloys containing a large percentage of chromium remain permanently bright in moist air: they can be prepared directly from purified chromite by the thermit process. Alloys of chromium, tungsten, and cobalt are extremely hard even at high temperatures, and are used in steel-cutting tools. Chromium is also used in nickel-chromium resistances (p. 800), and in plating the bright parts of motor cars, bath taps, and other metal articles. Chromium plating is usually carried out in a glass-lined tank with a lead anode, using a high current density. The electrolyte is a warm concentrated solution of chromic acid containing a little sulphuric acid. Since the chromium coating is slightly porous, the article to be plated is first given a coating of nickel.

CHROMIUM COMPOUNDS.—The salt-forming oxides of chromium are the *monoxide*, CrO, the *sesquioxide*, Cr_2O_3, and the *trioxide*, CrO_3.

The *monoxide* is a strongly basic oxide and corresponds with the chromous salts, which are not noticeably hydrolysed in solution, but are very readily oxidized to chromic salts, even by the air.

The *sesquioxide* is more weakly basic, and the chromic salts are hydrolysed in solution. The sesquioxide has also weakly acid properties, and when fused with bases forms a series of compounds called the chromites:

$$MgO + Cr_2O_3 = MgCr_2O_4.$$
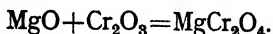
The soluble chromites are, however, decomposed by water.

The *trioxide* is a strongly acidic oxide, and is indeed chromic anhydride. From this oxide the chromates and dichromates are derived.

A series of unstable perchromates is also known, but the corresponding oxide, if it exists, has not been isolated.

OXIDES AND HYDROXIDES.

Chromium sesquioxide, Cr_2O_3.—The preparation of this compound from chromite has been described: it can be prepared in a state of purity by heating ammonium dichromate:

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2\uparrow + 4H_2O\uparrow.$$
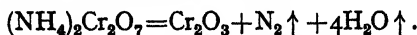
If once started the reaction goes on by itself, and this is the basis of the well-known 'volcano' experiment, in which a heap of ammonium dichromate is ignited by a red-hot wire thrust into it.

Chromium sesquioxide as thus prepared is a voluminous green powder insoluble in water; it has been used as a pigment. It is very difficult to reduce, but can readily be oxidized to a chromate by fusion with a base and an oxidizing agent such as potassium permanganate. Its rate of solution in acids, like that of many other metallic oxides, depends on the temperature to which it has been heated, and if it has been strongly ignited is very small. Associated wity varying amounts of water, it is precipitated as a jelly from chromic solutions by alkalis, but dissolves in excess. This is not due to the formation of a chromite (which cannot exist in aqueous solution), as can be shown by dialysis, which separates the whole of the sesquioxide; the alkaline solutions are in fact colloidal. The sesquioxide is also precipitated from such alkaline solutions by boiling or even on long standing. If ammonia is added to chromic solutions the same precipitate is thrown down, but it dissolves in excess of ammonia with a violet colour due to a complex chromium-ammonia ion.

Chromium dioxide, CrO_2, is prepared by heating the hydroxide in oxygen; on strong heating it decomposes into the sesquioxide and oxygen. It can be precipitated from cold solutions of a chromate and a chromic salt:

$$CrO_4'' + 2Cr''' + 2H_2O = 3CrO_2 \downarrow + 4H',$$

a reaction which supports the view that it is a compound of the basic sesquioxide and the acidic trioxide—$Cr_2O_3.CrO_3$. It is decomposed by boiling water into the sesquioxide and chromic acid:

$$Cr_2O_3.CrO_3 + H_2O = Cr_2O_3 + H_2CrO_4.$$
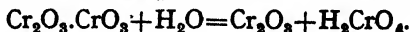
Chromous oxide, CrO, is best prepared by warming chromium amalgam with dilute nitric acid, which dissolves the mercury and oxidizes the chromium. It is a black powder which may inflame in the air, forming the sesquioxide. *Chromous hydroxide*, $Cr(OH)_2$, can be precipitated from chromous solutions by alkalis, but the oxide cannot be obtained by removing the elements of water from this substance, which loses hydrogen on heating:

$$2Cr(OH)_2 = Cr_2O_3 + H_2 \uparrow + H_2O \uparrow.$$
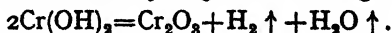
Chromium trioxide, CrO_3.—Beautiful scarlet needles of this substance are precipitated when concentrated sulphuric acid is added to the concentrated solution of a dichromate:

$$H_2Cr_2O_7 - H_2O = 2CrO_3 \downarrow.$$

They are washed with concentrated nitric acid and dried by warming. The trioxide melts at 196° and on stronger heating is converted to the sesquioxide with loss of oxygen. It is very soluble in water, forming dichromic acid, $H_2Cr_2O_7$, and in the solid state or in solution is a powerful oxidizing agent. With organic substances such as paper or alcohol the reaction may be violent.

CHROMIC COMPOUNDS.—Solution of these compounds, which contain tervalent chromium, may be obtained by dissolving the sesquioxide in acids, or the metal in acids in the presence of air, or by reducing chromate or dichromate solutions with, say, sulphur dioxide:

$$Cr_2O_7'' + 3SO_2 + 2H' = 2Cr''' + 3SO_4'' + H_2O.$$
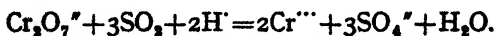
These solutions may be green or violet according to the temperature and the concentration. They have an acid reaction from hydrolysis if they contain anions of a strong acid. The varying colours are attributed to the existence of different complex cations in which the chromium has a covalency of six and is associated with molecules of water and sometimes with the acidic element or radical of the salt: this will be discussed more fully under chromic chloride.

Chromic chloride, $CrCl_3$, may be obtained in solution by the methods just described. The anhydrous salt is obtained by the

action of chlorine on the metal at 600°, or by heating in chlorine a mixture of the sesquioxide and carbon, or by heating the sesquioxide alone in the vapour of sulphur chloride. It is a violet crystalline substance with a high melting-point, which on heating in the air loses chlorine and is converted to the sesquioxide.

The anhydrous salt will dissolve in water only in the presence of small traces of other substances, such as chromous salts. The anhydrous substance can be recovered from the solution by evaporating to dryness in a current of hydrogen chloride.

Dilute aqueous solutions of chromic chloride are violet, concentrated solutions green, though the change from one form to the other is not always rapid. Moreover, precipitation experiments with silver salts show that while the whole of the chloride can be immediately precipitated from the violet solutions, the green solutions yield only one-third of their chlorine. BJERRUM succeeded in isolating from the solutions a third substance, pale green in colour, from whose solutions two-thirds of the chloride could be precipitated. The cations present in these solutions are therefore formulated:

$$[CrCl_2.4H_2O]^{\cdot} \quad dark \; green$$
$$[CrCl.5H_2O]^{\cdot\cdot} \quad pale \; green$$
$$[Cr.6H_2O]^{\cdot\cdot\cdot} \quad violet$$
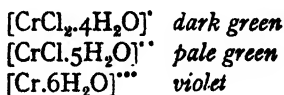
It is only to be expected that dilution should favour the formation of the violet form:

$$[CrCl_2.4H_2O]^{\cdot} + 2H_2O \rightleftharpoons [Cr.6H_2O]^{\cdot\cdot\cdot} + 2Cl',$$
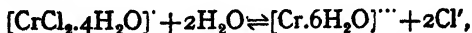
and the reverse change tends to take place on heating. All these solutions deposit the same chromic hydroxide on treatment with alkali.

Chromic bromide, $CrBr_3$, shows a somewhat similar behaviour in solution, and can be prepared by similar methods.

Chromic sulphate, $Cr_2(SO_4)_3$.—This substance is obtained by dissolving chromic hydroxide in hot concentrated sulphuric acid and allowing the solution (at first green) to stand, when it becomes violet and deposits violet crystals of the hydrated sulphate. All the water may be driven off by heating in the air, leaving the violet anhydrous compound, readily soluble in water. Solutions of chromic sulphate may be either violet or green and may precipitate the whole or only a part of the contained sulphate radical on treatment with barium solutions: they undoubtedly owe their peculiar properties to complex ions, but the nature of these is still uncertain.

Potassium chromium sulphate, ' chrome alum,'

$$K_2SO_4.Cr_2(SO_4)_3.24H_2O.$$

This well-known member of the alum family is a by-product of the

manufacture of alizarin, and may be obtained by reducing a solution of potassium dichromate in dilute sulphuric acid with sulphur dioxide, when it is precipitated in large purple crystals, readily soluble in water. Chrome alum is a double and not a complex salt, and its solutions have the peculiarities of solutions of chromic sulphate.

Chromic sulphide, Cr_2S_3, cannot be prepared in the wet way, as the addition of a sufficient concentration of sulphide ions to chromic solutions leads to the precipitation of the hydroxide:

$$2Cr^{\cdots}+3S''+6H_2O=2Cr(OH)_3\downarrow+3H_2S\uparrow.$$
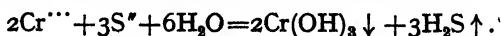
This must be carried out in alkaline solution, since in acid solution the sulphide ion concentration is inadequate. In the dry way the compound may be prepared by heating the sesquioxide in hydrogen sulphide, or in carbon disulphide vapour.

Chromic nitrate, $Cr(NO_3)_3$, has not been prepared in the anhydrous condition, as the hydrates are decomposed by heat. Various hydrates can be prepared from the solution obtained by dissolving chromic hydroxide or chromium sesquioxide in nitric acid.

Chromic carbonates.—The addition of carbonate solutions to chromic solutions leads to the precipitation of light green basic carbonates. The anhydrous carbonate has not been prepared.

Chromammines.—By treating chromium compounds under suitable conditions with ammonia, often in company with ammonium chloride, a large number of chromammines can be prepared, compounds containing a complex cation in which the chromium atom has a covalency of six and is associated with from one to six molecules of ammonia. Thus *chloropentammino chromic chloride*, $[CrCl.5NH_3]Cl_2$, is prepared by the action of liquid ammonia on anhydrous chromic chloride, and by the action of a little water on this compound, *chloroaquotetrammino chromic chloride*. $[CrCl.H_2O.4NH_3]Cl_2$, is derived. These compounds strongly recall the cobaltammines (p. 349).

CHROMOUS COMPOUNDS.—These are obtained by dissolving chromium in acids (e.g. dilute sulphuric acid) in the absence of air, but this is an inconvenient method, and the energetic reduction of chromic salts is better. Chromous solutions are sky-blue in colour and are not markedly hydrolysed, but are very readily oxidized even by the air, since the oxidation potential of the change $Cr^{\cdots}\rightarrow Cr^{\cdot\cdot}$ is -0.4 volt. They have been used as powerful reducing agents and for the removal of oxygen from mixtures of gases.

Chromous chloride, $CrCl_2$.—The anhydrous compound, prepared by heating anhydrous chromic chloride in hydrogen, is colourless, and dissolves freely in water to form a blue solution. This is more

readily prepared by reducing a solution of potassium dichromate with zinc and hydrochloric acid. In preparing chromous solutions it is important first to remove all dissolved air from the reagent solutions by prolonged boiling or by warming under reduced pressure. From concentrated solutions of chromous chloride, prepared from chromous acetate (see below), the tetrahydrate $CrCl_2.4H_2O$ can be precipitated with gaseous hydrogen chloride, and on cautious warming in an inert gas this yields the anhydrous compound. The density of the vapour obtained by heating this substance to a high temperature shows that, even at 1300°, the mean molecular weight is nearly double that required by the formula $CrCl_2$.

Chromous acetate, $Cr(CH_3.COO)_2.H_2O$. — By adding sodium acetate to the crude solution of chromous chloride prepared in the manner just described, it is possible to precipitate this compound in red crystals, which by treatment with acids can be used for the preparation of other chromous salts.

Chromous sulphate, $CrSO_4.7H_2O$, crystallizes as blue crystals from solutions which can be prepared by the methods already described.

CHROMITES.—These compounds, analogues of spinel (p. 535), cannot be prepared by dissolving chromium sesquioxide in caustic alkalis, as the solutions thus obtained can be shown by dialysis to be colloidal. The soluble chromites are decomposed by water, but stable compounds can be produced by fusing basic oxides with chromium sesquioxide (e.g. magnesium chromite, p. 705), or by fusing the chloride of the metal with potassium dichromate and extracting the product with concentrated hydrochloric acid, e.g.:

$$2BaCl_2+2K_2Cr_2O_7=2BaCr_2O_4+4KCl+3O_2\uparrow.$$
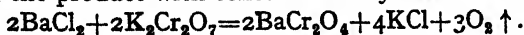
CHROMATES AND DICHROMATES.—Chromium trioxide dissolves freely in water with evolution of heat. Salts are known derived from two acids corresponding with this oxide, *chromic acid*, H_2CrO_4, and *dichromic acid*, $H_2Cr_2O_7$. The chromates are yellow in solution, the dichromates orange, and chromate solutions are slightly alkaline while dichromate solutions are slightly acid. The chromates are converted to dichromates by the addition of acids, and these are reconverted into chromates by alkalis. Neither chromic nor dichromic acid can be isolated from solutions of chromium trioxide, for on evaporation to dryness decomposition takes place with loss of oxygen, and the final product is the sesquioxide.

The equilibrium in solution between chromates and dichromates is most naturally represented by the equation:

$$2CrO_4''+H\cdot \rightleftharpoons Cr_2O_7''+OH',$$
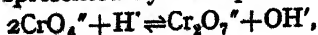
which explains the action of acids and alkalis and the hydrolysis

of the solutions.   Careful spectroscopic examination of the solutions shows that this is only part of the truth.   The predominating ion in solutions of dichromates is the *bi*chromate ion $HCrO_4'$, produced by hydrolysis:

$$Cr_2O_7'' + H_2O \rightleftharpoons 2HCrO_4',$$
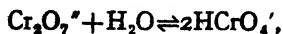
and the *di*chromate ion Cr_2O_7'' is present in large proportion only in concentrated solutions.   Nevertheless the solid dichromates contain the ion Cr_2O_7'', and the term ' dichromate ' should be applied to them, since the prefix ' bi- ' by long usage indicates an acid salt—that is, an acid in which not all the replaceable hydrogen has been replaced—such as sodium hydrogen carbonate, ' sodium bicarbonate,' $NaHCO_3$.

In the presence of acids dichromates are powerful oxidizing agents, and each dichromate ion liberates three atoms of oxygen:

$$Cr_2O_7'' + 8H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + 4H_2O + 3O$$
or $$2HCrO_4' + 8H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + 5H_2O + 3O.$$
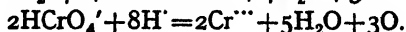
Dichromates will liberate chlorine from hot concentrated hydrochloric acid, and will oxidize bromides, iodides, sulphites, hydrogen sulphide (to sulphur), ferrous salts, and many other reducing substances.   In the titration of ferrous salts with dichromates potassium ferricyanide was formerly used as external indicator, but the discovery that diphenylamine can be used as an internal indicator has greatly improved the process.

Oxidation of certain organic compounds—e.g. ethyl alcohol—by dichromates is much affected by light.

The chromates are obtained by the oxidation of chromic compounds in the presence of a base, either in the fused state (at these temperatures the oxidation can be carried out with air) or in solution.   The only soluble chromates are those of the alkali-metals, ammonium, and the alkaline-earth metals, including magnesium, but with the exception of barium.   Since chromic acid is a weak acid, many chromates insoluble in water will dissolve in solutions of strong acids, which convert them to dichromates. Soluble chromates are poisonous.

Potassium chromate, K_2CrO_4, is prepared on the large scale by fusing chrome iron ore with caustic potash and potassium nitrate and extracting the product with water.   It is a yellow substance, melting at $970°$ and very soluble in water.

Potassium dichromate, $K_2Cr_2O_7$, is prepared by roasting the ore with lime and potassium carbonate.   The product is extracted with water and more potassium is added in the form of sulphate; the liquid is then made acid with sulphuric acid and evaporated.   The resulting potassium dichromate can easily be purified by recrystal-

lization, since it is very soluble in hot but not very soluble in cold water, and is supplied nearly pure for use in photography. It is an orange substance, melting at about 400°, which on very strong heating yields the chromate, chromium sesquioxide, and oxygen:

$$4K_2Cr_2O_7 = 4K_2CrO_4 + 2Cr_2O_3 + 3O_2 \uparrow.$$

Its solutions are much used in volumetric analysis as oxidizing agents, and have certain advantages over permanganates; thus they are unchanged on keeping, do not affect rubber, and can safely be used in cold dilute hydrochloric acid. They can be prepared from a known weight of pure fused potassium dichromate.

Ammonium dichromate, $(NH_4)_2Cr_2O_7$.—The decomposition of this substance by heat has been described (p. 705).

Sodium chromate and **sodium dichromate** resemble the potassium salts, but are still more soluble in water. The latter salt is used in tanning leather.

Barium chromate, $BaCrO_4$, is a lemon-yellow substance prepared by precipitation: it is almost insoluble in water but freely soluble in strong acids. As the chromate of calcium is soluble in water, this substance is used in the separation of barium in analysis.

Lead chromate, $PbCrO_4$, occurs in nature as *crocoisite* (p. 703), and is prepared by precipitation as a bright yellow substance which, under the name of 'chrome yellow,' is used as a pigment. It is highly insoluble in water but soluble in acids, and is sometimes used in the analysis of lead compounds.

Silver chromate, Ag_2CrO_4, is a brick-red substance prepared by precipitation. If a drop of a silver nitrate solution is placed on a layer of gelatine containing potassium chromate in solution and spread on a glass plate, the precipitate forms in concentric rings separated by clear spaces. They are called 'LIESEGANG'S rings' after their discoverer. The exact explanation of this curious experiment has been much debated.

Potassium chlorochromate, $CrO_2.Cl.OK$.—This substance is deposited in red-brown crystals from solutions of potassium dichromate in warm concentrated hydrochloric acid:

$$Cr_2O_7'' + 2HCl = 2CrO_3Cl' + H_2O.$$
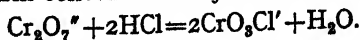
With sulphuric acid it yields chromyl chloride, and is intermediate between potassiam chromate and that compound:

chromate   chlorochromate   chromyl chloride
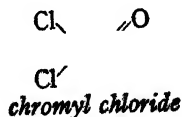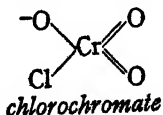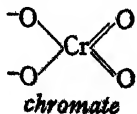
Chromyl chloride, CrO_2Cl_2.—This substance is prepared by distilling a dichromate and a chloride with concentrated sulphuric acid. The product contains hydrogen chloride and chlorine, from which it may be freed by one or two further distillations. It may also be prepared by the addition of concentrated sulphuric acid to a well-cooled mixture of chromium trioxide and concentrated hydrochloric acid. The chromyl chloride forms a lower layer and may be separated.

$$CrO_3 + 2HCl = CrO_2Cl_2 + H_2O.$$
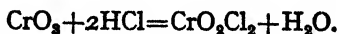
Chromyl chloride is a heavy liquid, density 1·96, with a splendid deep red colour, freezing at $-96°$ and boiling without decomposition at 117°. It is a purely covalent compound soluble in organic liquids such as carbon tetrachloride; its solutions in these solvents are scarcely affected by sodium in the cold. It is immediately decomposed by water with the formation of chromic and hydrochloric acids, being indeed the acid dichloride of chromic acid:

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$
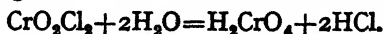
For this reason it fumes in moist air. It is a powerful oxidizing and chlorinating agent which has found practical use in organic chemistry, and, if added in the pure state to easily oxidizable substances such as alcohol or phosphorus, produces inflammation or explosion.

Chromyl fluoride, CrO_2F_2, is a similar substance obtained by heating lead chromate with calcium fluoride and sulphuric acid. The corresponding bromide and iodide are unknown, and this has been suggested as a method of separating chlorine from the heavier halogens.

Perchromates.—When hydrogen peroxide is added to an acid solution of a dichromate the liquid becomes blue, and the coloured compound can be extracted with ether, in which it forms a deep blue solution. This is a very sensitive test either for dichromates or for hydrogen peroxide. The blue substance is not a perchromic acid, but an oxide CrO_5, which by the addition of pyridine is converted into the compound py$\rightarrow CrO_5$, insoluble in water. From this blue solid alkalis release pyridine, but the remaining CrO_5 is completely decomposed, and no salt is formed. The constitution of the oxide CrO_5 is still uncertain, but it is almost certainly a peroxide. From *alkaline* chromate solutions hydrogen peroxide forms true perchromates, as red solids, M_3CrO_8.

MOLYBDENUM

Mo $= 95·95$. *Atomic Number,* 42

History.—Although there is no doubt that molybdenum minerals were known even as early as the fourth century B.C., they were confused with galena and graphite, and it was not until 1778 that

SCHEELE showed that *molybdenite* (MoS$_2$) is a compound of sulphur with a metal. The metal itself was isolated by HJELM in 1782, and was called *molybdenum*.

Occurrence and Extraction.—Molybdenum is one of the less common metals, but small quantities of its ores occur in many parts of the world. The principal ores are *molybdenite*, MoS$_2$, from Australia, Austria, and elsewhere, and *wulfenite* (lead molybdate), PbMoO$_4$, from Austria, Siberia, and the United States.

Molybdenite is roasted in air, and the trioxide, MoO$_3$, thus obtained is dissolved in ammonia, the product being ammonium molybdate, (NH$_4$)$_2$MoO$_4$. This is purified by processes depending on the nature of the elements to be eliminated, and is then converted to the trioxide, MoO$_3$, by heating. From this substance the metal may be prepared by the Goldschmidt process (p. 533).

Properties.—Molybdenum is a hard white metal with a very high melting-point (about 2620°). It is added in small quantities to steel to improve the tensile strength, and is also used in certain alloys to increase the magnetic retentivity. On account of its resistance to high temperatures, it is used for the filament supports of amplifying valves.

Molybdenum is slowly oxidized when heated in the air, and can be burned in oxygen at a red heat. It does not readily dissolve in most acids, but nitric acid of intermediate concentration dissolves it without difficulty.

OXIDES AND HYDROXIDES.—Molybdenum sesquioxide, Mo$_2$O$_3$, like chromium sesquioxide, is weakly basic, the dioxide, MoO$_2$, probably corresponds with no series of salts, and the trioxide, MoO$_3$, like chromium trioxide, is strongly acidic.

Molybdenum sesquioxide, Mo$_2$O$_3$, is obtained in the hydrated condition by reducing the other oxides or a molybdate solution, often with zinc and sulphuric acid. The addition of an alkali to the solution precipitates the *trihydroxide*, Mo(OH)$_3$, as a brown powder, and it is doubtful whether the anhydrous oxide can be prepared. The hydroxide dissolves in acids to give purple solutions of salts such as MoCl$_3$ or Mo$_2$(SO$_4$)$_3$. It is not, however, possible to isolate these salts by evaporation of the solution, as hydrolysis takes place.

Molybdenum dioxide, MoO$_2$, may be obtained by gentle oxidation of the sesquioxide, or by reducing hydrated molybdenum trioxide (molybdic acid), as for instance with hydrogen. It is a grey substance which will not dissolve in acids, except nitric acid, which oxidizes it.

Molybdenum trioxide, MoO$_3$, is obtained, as already described, by roasting the sulphide in air. It may be prepared in a state of purity by heating ammonium molybdate, purified by several

recrystallizations, first alone, then in a stream of oxygen. It is a white fine powder like talc, which on very strong heating sublimes. It dissolves in water, forming molybdic acid, of which the simplest formula is H_2MoO_4, and in alkalis to form molybdate solutions. It may also, if it has not been heated to too high a temperature, dissolve in acids, yielding molybdenoxyl compounds, such as $MoO(OH)_2Cl_2$ with hydrochloric acid, and MoO_2SO_4 with sulphuric acid.

Molybdates.—The molybdic acids form several series of salts of great complexity. Solutions of the monomolybdates, which perhaps contain the ion MoO_4'', readily yield more highly condensed substances. *Ammonium paramolybdate* is obtained by evaporating a solution of the trioxide in ammonia, and has the formula $(NH_4)_6Mo_7O_{24}.4H_2O$. It is soluble in water, and the solution in dilute nitric acid is used in the detection of soluble phosphates, with which a bright yellow precipitate of ammonium phospho-molybdate is thrown down. After heating, this compound has a composition which may be represented as $(NH_4)_3PO_4.12MoO_3$. From the nitric acid solution of ammonium paramolybdate there separates a white precipitate of molybdenum trioxide, associated with varying amounts of water, so the solution should always be freshly made up when required for analysis. The simple *ammonium monomolybdate*, $(NH_4)_2MoO_4$, may be obtained by evaporation of a solution of ammonium paramolybdate in excess of ammonia.

Molybdic acid and the molybdates are weak oxidizing agents which will liberate iodine from acid iodide solutions, being themselves reduced to a molybdenum oxyiodide, MoO_2I, in which the molybdenum is quinquevalent:

$$2MoO_4''+4I'+8H^{\cdot}=2MoO_2I+I_2+4H_2O.$$
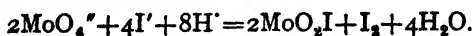
HALIDES.—**Molybdenum hexafluoride,** MoF_6, is produced by the union of the elements, and may be compared with the similar compounds of tungsten and uranium. It is a white solid, melting at 17°, and is decomposed by water.

Molybdenum dichloride, $(MoCl_2)_6$, is obtained by heating the tri-chloride in an inert atmosphere, when the tetrachloride distils off, leaving behind a yellow powder, without reducing properties, and of composition $(Mo_6Cl_8)Cl_4$, the bracketed group being a complex cation, whose unique nature has been revealed by X-ray methods. The valency of the contained molybdenum is uncertain.

Molybdenum trichloride, $MoCl_3$, is obtained in solution by reducing a solution of molybdenum trioxide in hydrochloric acid. The solution is decomposed by boiling. The anhydrous salt may be prepared by reducing the pentachloride in hydrogen, but when prepared in this way it will not dissolve in water.

Molybdenum pentachloride, $MoCl_5$, is prepared by the action of chlorine on warm molybdenum. It is a deliquescent substance, melting at 194° and boiling at 268°; its solutions in water are unstable.

Permolybdates.—The addition of hydrogen peroxide to acid molybdate solutions produces a yellow colour but no molybdenum compound is extracted by ether.

Molybdenum blue, see p. 717.

TUNGSTEN

$W = 183.86$. *Atomic Number,* 74

History.—AGRICOLA, in the sixteenth century, mentioned a mineral called *lupi spuma*, a name that he derived from the German *wolfram*, i.e. ' wolf-froth ' ($FeWO_4$ mixed with $MnWO_4$). From a somewhat similar mineral, now known as *scheelite* ($CaWO_4$), Scheele in 1781 obtained lime and a new metallic acid. Two years later, the brothers DE ELHUYAR, possibly acting on Scheele's direction, showed that wolfram contains the same metallic acid as scheelite, but associated with iron and manganese instead of with calcium. They succeeded in isolating the oxide of the new metal, and on reduction with charcoal this yielded the metal, *tungsten*. It is likely that Scheele himself independently discovered a method of isolating tungsten, perhaps before the Spaniards had done so.

Occurrence and Extraction. — Tungsten is not an abundant element: its most important ore is *wolframite*, a mixture of the isomorphous tungstates of iron and manganese, $FeWO_4$ and $MnWO_4$. There are important deposits of this mineral in Russia, Spain, the United States, and elsewhere. Another important ore is *scheelite*, or calcium tungstate, $CaWO_4$, which is found in the Malay Peninsula. These minerals are crushed and roasted; sodium carbonate is added either before or after the roasting, and the product is extracted with water, in which sodium tungstate dissolves while most of the impurities do not. The addition of acids to these solutions precipitates hydrated tungsten trioxide, WO_3, which is washed and dried. The reduction of this oxide to the metal, though difficult, is less so than the reduction of the corresponding oxides of chromium and molybdenum; it may be carried out either by the thermit process, by reduction with carbon, or by electrolysis of a solution of tungstic acid in a fused mixture of alkali-metal chlorides. If the thermit process is used, an excess of aluminium must be avoided, or some of it will be found in the product, on whose properties it has a deleterious effect. A useful tungsten-iron alloy can be prepared by the reduction with aluminium powder of mixed oxides

of tungsten and iron. Such alloys, often containing chromium as well, are used for cutting-tools, and an alloy of tungsten, cobalt, and chromium is used in the manufacture of surgical instruments. The principal use of tungsten is, however, the manufacture of filaments for electric-light bulbs.

Tungsten Filaments.—The earliest filaments for use in these bulbs were made from carbon. The first inventor to make a lamp with a satisfactory metal filament was AUER VON WELSBACH, whose discovery of the incandescent gas-mantle has already been mentioned (p. 597). The original metal filaments were made from the rare metal osmium, but they were very fragile, and the high cost of osmium (at that time about £100 per lb.) was a serious disadvantage. The great obstacle to the use of tungsten filaments was the difficulty of drawing the metal into wires, for tungsten, as obtained by all processes except the electrolytic, is a most refractory powder, melting at over 3000°, the highest melting-point of all known metals except rhenium. The modern process is approximately as follows. The powder is compressed into very brittle—indeed fragile —bars in a hydraulic press, and the bars are then heated several times to 2000° in an electric furnace in an atmosphere of hydrogen. After this heat treatment the metal is fairly malleable, but while the wire is being drawn it is constantly hammered. The filaments produced in this way are very tough, though they are only about one-fortieth of the diameter of a human hair. The emitting filaments of amplifying valves are usually made from tungsten coated with barium oxide, which improves the electron emission.

Properties.—Tungsten is a hard white metal which will take a high polish. Its melting-point (3370°) is extremely high, and it is this fact, combined with its indifference to nitrogen at all temperatures, that has led to its use in filaments. Moreover, the resistance of a tungsten filament increases with the temperature, whereas that of a carbon filament diminishes, so that the current through tungsten lamps is much steadier than through carbon lamps. Modern filaments work at so high a temperature (up to 2500°) that even tungsten tends to volatilize, but it is found that the volatilization can be reduced by filling the bulb with nitrogen or argon instead of evacuating it.

Tungsten is oxidized when heated in the air, and will decompose steam at a red heat, but it is even less readily dissolved by acids than is molybdenum. It can, however, be dissolved by fused alkalis or fused oxidizing agents.

ES AND HYDROXIDES.

Tungsten dioxide, WO_2, is prepared by heating the trioxide in hydrogen, or by reducing tungstate solutions with zinc and

hydrochloric acid. The corresponding *hydroxide*, $W(OH)_4$, has been prepared by electrolytic reduction of tungsten solutions. Both substances are insoluble in water and are powerful reducing agents. They are soluble in some acids and yield reducing solutions which contain quadrivalent tungsten salts.

Blue oxides of molybdenum and tungsten.—It has long been known that the first product of the gentle reduction of the trioxides of molybdenum or tungsten is often seen as a deep-blue solution or a blue-black solid, easily soluble in water. Similar blue compounds result from the mild oxidation of compounds in lower valencies as a penultimate stage in the final formation of the trioxide. Such products are found to contain metal and oxygen in atomic proportions between $1 : 2.5$ and $1 : 3$ and they are approximately represented by a formula M_4O_{11}. As they are amorphous and afford no definite X-ray pattern their constitution remains obscure. It is plausible to assume that these blue oxides are members of a limited range of solid solutions of trioxide MoO_3 and pentoxide Mo_2O_5.

Tungsten trioxide, WO_3, is obtained, as already described, from tungsten ores, and may be prepared in a state of purity by strongly heating ammonium tungstate in the air. It is a dense yellow powder, insoluble in water or acids, but soluble in alkaline solutions to form the tungstates. It is unchanged by heating to a high temperature in the air.

Tungstic acid and the Tungstates.—*Tungstic acid* is precipitated when solutions of the tungstates are acidified; the formula may be H_2WO_4 (yellow), or H_4WO_5 (white), according to the temperature. If these substances are heated, water is given off and the trioxide remains. Tungstic acid resembles molybdic acid in the formation of a large number of condensed salts. Two of the more definite classes are the *normal tungstates*, derived from H_2WO_4, and the *metatungstates*, $M_6(H_2W_{12}O_{40}).xH_2O$. The normal tungstates of the alkali-metals and magnesium are soluble in water; the other normal tungstates are nearly insoluble. The tungstates have little or no oxidizing power.

HALIDES.—**Tungsten hexafluoride,** WF_6, prepared from tungsten hexachloride and antimony trifluoride, is colourless, reacts with water, and fumes in the air; it boils at $19.5°$.

Tungsten dichloride is obtained by reduction of the higher chlorides, but like the corresponding compound of molybdenum probably does not possess the simple formula. It is a powerful reducing agent decomposed by air or water (cf. p. 714).

Tungsten trichloride is unknown, but by reducing a solution of a tungstate of an alkali-metal with tin and hydrochloric acid a stable series of salts such as $K_3W_2Cl_9$ can be prepared. Concentrated

solutions are green, but the dilute ones are yellow. These solutions contain tervalent tungsten and are strong reducing agents.

Tungsten tetrachloride, WCl_4, is obtained by cautious reduction of the higher chlorides with hydrogen. It is a brown solid which when heated yields the dichloride and pentachloride, and is decomposed by water with formation of the dioxide.

Tungsten pentachloride, WCl_5, is obtained by distilling the hexachloride. It is a grey solid, melting at 250° and boiling at 275°, and with water yields the blue oxide.

Tungsten hexachloride, WCl_6, is the highest chloride of the metal, and is produced by union of the elements in the absence of air. It is a violet substance, melting at 275° and boiling at 346°. The density of the vapour shows it to be partially dissociated, probably into the pentachloride and chlorine. When exposed to moist air it forms a volatile oxychloride, $WOCl_4$, and is violently hydrolysed by water, yielding finally the hydrated trioxide, WO_3.

Pertungstates.—These compounds resemble the permolybdates.

URANIUM

U$=238 \cdot 07$.   *Atomic Number*, 92

History.—The discovery of uranium is due to KLAPROTH, who in 1789 showed that it was contained in the mineral *pitchblende*. The name *uranium* was given to the new metal in commemoration of HERSCHEL's discovery of the planet Uranus a few years earlier (1781). Klaproth believed himself to have isolated metallic uranium, but PÉLIGOT (1842) proved that Klaproth's 'uranium' was really an oxide, from which the metal could be extracted by further reduction. The observation that uranium salts are radioactive—an observation that led to the discovery of radium—was made by BECQUEREL in 1896.

Occurrence and Extraction.—Uranium is a scarce element, and its ores are also processed for the still scarcer element radium (p. 304): uranium itself is required for the modern projects of utilizing atomic energy. The chief source of uranium and radium is now the deposit of pitchblende, containing U_3O_8, discovered in 1930 at the Great Bear Lake in Canada. Before this discovery the richest known deposits were in the Belgian Congo. The radioactive relations of uranium have already been described (p. 308).

The uranium ore is intimately mixed with sodium carbonate and heated in a reverberatory furnace. The uranium is now present as sodium uranate, which can be extracted with dilute sulphuric acid. At this point the barium and radium separate out as insoluble sulphates. Other impurities are precipitated from the solution by

the addition of sodium carbonate, which leaves the uranium in solution as sodium uranyl carbonate. This solution is acidified and evaporated, and sodium diuranate, $Na_2U_2O_7.6H_2O$, is obtained as a yellow solid. Alternatively the solution may be boiled with ammonium sulphate, which precipitates ammonium diuranate, $(NH_4)_2U_2O_7$, from which urano-uranic oxide, U_3O_8, can be obtained by strong heating.

The preparation of metallic uranium is difficult. Urano-uranic oxide may be reduced with carbon or magnesium or calcium in the electric furnace, or uranium tetrachloride, UCl_4, may be heated with sodium in a steel bomb.

Properties.—Metallic uranium is a fairly hard white metal which will take a high polish. It is malleable, ductile, and has a melting-point (1150°) very much lower than those of the other metals of the sub-group (cf. tungsten, 3370°). The metal is much more reactive than tungsten. It tarnishes in the air and readily burns when heated. It liberates hydrogen from dilute acids, and precipitates the more electronegative metals from solutions of their salts.

OXIDES AND HYDROXIDES.—The principal oxides of uranium are the basic *uranous oxide*, UO_2, corresponding with the uranous salts, the intermediate *urano-uranic oxide*, U_3O_8, with which no series of salts corresponds, and the amphoteric *trioxide*, UO_3.

Uranous oxide, UO_2, is obtained by heating urano-uranic oxide in hydrogen, and is a stable substance which may be black, brown, or red according to the method of preparation employed; the above method yields a black product. It may also be prepared by heating sodium uranate with sodium chloride and charcoal, and washing soluble impurities from the product with dilute acid. When gently heated in the air it takes up oxygen and is converted to urano-uranic oxide, but on strong heating the lower oxide is regained. It dissolves in acids only with difficulty, but by nitric acid is readily converted to uranyl nitrate, $UO_2(NO_3)_2$. It is a weak reducing agent which will precipitate silver from ammoniacal solutions of its salts, being itself converted to the trioxide. *Uranous hydroxide*, $U(OH)_4$, is precipitated from uranous solutions by alkalis, and readily dissolves in acids. It is oxidized by the air, and uranous solutions are reducing agents.

Urano-uranic oxide, U_3O_8, is found in nature, as already described, but may be artificially prepared by heating either the higher or the lower oxides to a moderate temperature in the air. It dissolves in acids, though with reluctance, to form solutions which contain both uranous and uranyl salts:

$$U_3O_8 + 8H^{\cdot} = U^{\cdots\cdot} + 2UO_2^{\cdot\cdot} + 4H_2O.$$
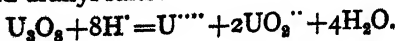
Uranium trioxide, UO_3, is best obtained by gently heating ammonium diuranate:

$$(NH_4)_2U_2O_7 = 2UO_3 + 2NH_3\uparrow + H_2O\uparrow$$
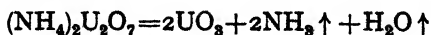
(compare ammonium dichromate). It is a red or yellow substance which yields urano-uranic oxide on heating. It forms hydrates $UO_3.H_2O$ and $UO_3.2H_2O$, which may also be represented as H_2UO_4 and H_4UO_5 (different forms of *uranic acid*), and dissolves readily in alkalis to form uranates. It also has weakly basic properties, but these are confined to the formation of uranyl salts containing the ion $UO_2^{\cdot\cdot}$:

$$UO_3 + 2H^{\cdot} = UO_2^{\cdot\cdot} + H_2O.$$

Uranic acid and the Uranates.—The uranic acids are obtained by dissolving the trioxide in water or by the hydrolysis of the uranyl compounds. In addition to the normal acid H_2UO_4, other condensed acids exist, but the compound $H_2U_2O_7$, from which the stable diuranates are derived, is itself unknown. These diuranates are often prepared by precipitating a uranyl solution with a base:

$$2UO_2^{\cdot\cdot} + 6OH' = U_2O_7'' + 3H_2O.$$
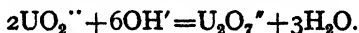
The uranates are insoluble in water, even those of sodium, potassium, and ammonium. They are stable substances with little or no oxidizing action.

Uranyl salts.—These salts, which contain the ion $UO_2^{\cdot\cdot}$, are prepared by dissolving the trioxide in acids, or by oxidizing solutions of uranous salts, e.g. by boiling with nitric acid:

$$U^{\cdots\cdots} + O + H_2O = UO_2^{\cdot\cdot} + 2H^{\cdot}.$$
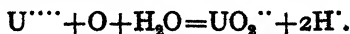
Such uranyl compounds as the halides, sulphate, or nitrate are readily soluble in water, but the solutions are much hydrolysed, are strongly acid, and may deposit basic salts or even uranic acid on evaporation.

Halides.—In these compounds uranium shows all valencies from three to six, the highest being seen in the *hexachloride*, UCl_6, and in the *hexafluoride*, UF_6. This substance, together with the *tetrafluoride*, UF_4, is produced by the action of fluorine on the pentachloride. It is pale yellow, sublimes at $56°$, is decomposed by water and chemically reactive. The tetrafluoride, on the other hand, is an insoluble substance precipitated from uranous solutions by soluble fluorides, and is sometimes used in the analysis of uranium compounds. It has a high melting-point (about $1000°$) and appears to be a true salt, while the hexafluoride is covalent.

Combination of uranium and chlorine leads to the formation of the *tetrachloride*, UCl_4, together with a little of the more volatile *pentachloride*, UCl_5. A heated mixture of the oxide and carbon may be substituted for the metal. The tetrachloride forms beautiful dark green crystals, which on strong heating form a red vapour. It is very deliquescent and dissolves freely in water. Its solution is hydrolysed and has a strong acid reaction; it is a powerful reducing agent on account of the facility with which it gives rise to uranyl compounds.

Uranium trichloride, UCl_3, is prepared by reducing the tetrachloride with hydrogen. It dissolves in water to form a red solution which has very powerful reducing properties, and slowly decomposes with evolution of hydrogen and formation of the tetrahydroxide, $U(OH)_4$.

Oxyhalide.—*Uranyl chloride*, UO_2Cl_2, is obtained by the action of chlorine on uranous oxide. It is a soluble yellow substance whose solutions can be prepared without difficulty by the oxidation of solutions of the tetrachloride, e.g. with nitric acid. The solution is hydrolysed and deposits uranic acid on keeping.

Uranous nitrate does not exist, since uranous compounds are oxidized by nitric acid, but

Uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, which results from attempts to prepare it, is a stable substance and the commonest compound of uranium. It is prepared from roasted uranium ores by dissolving them in nitric acid and recrystallizing. If required pure, it may be obtained from nitric acid and any oxide of uranium. The crystals, which are yellow in colour, give out flashes of light when crushed or shaken. Uranyl nitrate is extremely soluble in water and organic solvents. The aqueous solution contains the ions $UO_2^{..}$ and NO_3', but is much hydrolysed; the anhydrous salt can, however, be prepared by cautious evaporation of the solution under suitable conditions. It decomposes on heating.

Uranous sulphate, $U(SO_4)_2$ (hydrated), is prepared in solution from uranous oxide and sulphuric acid. The anhydrous compound is unknown, but there is a large number of hydrates. The solutions are hydrolysed and are reducing agents.

Uranyl sulphate, UO_2SO_4, is prepared from uranyl nitrate and concentrated sulphuric acid. It is soluble in water, and hydrates are known.

Uranous carbonate does not exist, since the hydrogen ion concentration of uranous solutions is sufficient to liberate carbon dioxide from carbonates.

Uranyl carbonate.—Only basic carbonates can be precipitated from uranyl solutions by soluble carbonates, but fairly stable double salts of the normal carbonate with the alkali-metal carbonates can be prepared.

Peruranates.—If hydrogen peroxide is added to a solution of uranyl nitrate, an insoluble pale yellow substance with the formula $UO_4.2H_2O$ is precipitated. If the solution is first made alkaline with caustic alkali, a solution is obtained supposed to contain a peruranate of an alkali-metal. The constitution of these compounds is uncertain.

GROUP VII

FLUORINE, CHLORINE, BROMINE, IODINE, MANGANESE, TECHNETIUM, RHENIUM

F $=19\cdot00$; *atomic number*, 9   Cl $= 35\cdot457$; *atomic number*, 17
Br $=79\cdot916$; *atomic number*, 35   I $=126\cdot91$; *atomic number*, 53
Mn$=54\cdot93$; *atomic number*, 25   Tc$= (99)$; *atomic number*, 43
Re$=186\cdot31$; *atomic number*, 75

$$\text{F—Cl}\begin{cases}\text{Mn—Tc—Re}\\ \text{Br — I}\end{cases}$$
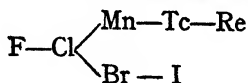
THIS is one of the extreme groups of the periodic table, and the re-semblance between the subgroups is very slight; it is indeed, confined to those compounds in which the elements of Subgroup A display their group valency of 7. Technetium and rhenium are discoveries of fairly recent years, and little is yet known of the former; manganese is thus the only reasonably abundant representative of Subgroup A. Its resemblances with the elements of Subgroup B (and the typical elements) are to be found in the heptoxide and the permanganates. These are isomorphous with the perchlorates, but the significance of this similarity can easily be exaggerated, and is diminished by the fact that the manganates are isomorphous with the sulphates, with which they have no periodic relationship.

Subgroup B, as might be expected, is closely connected with the typical elements (compare the alkali-metals), with which it forms a group of elements called the *halogens*.

THE HALOGENS

These elements display a very well-marked gradation of properties, though both the end members have several peculiarities.

	F	Cl	Br	I
Atomic Number	9	17	35	53
Atomic Weight	19·00	35·457	79·916	126·92
Atomic Volume	17·2	23·5	27·1	34·2
Ionic Radii (from crystal measurements; in Ångström units)	1·36	1·81	1·95	2·16
Melting-point	−223°	−102°	−7°	114°
Boiling-point	−188°	− 34°	59°	183°

As the atomic number increases the elements become less volatile, darker in colour, and chemically less active. The elements all exist in stable diatomic molecules whose tendency to dissociate into atoms on heating increases with the atomic number. The behaviour of their compounds is to a large extent controlled by the electrode potentials of the elements, which are (volts): F, $+2\cdot85$; Cl, $+1\cdot36$; Br, $+1\cdot065$; I, $+0\cdot535$. Thus each element will displace from binary compounds all elements to the right of it. Fluorine is the most powerful of all oxidizing agents, and with the exception of electrolysis in the absence of water no method is known of oxidizing fluorides to the element. Chlorine can be displaced from chloride solutions by strong oxidizing agents, whereas the liberation of bromine is easier, and of iodine easier still. The extreme electro-negative character of fluorine, connected with its unit negative valency and fairly low atomic volume, leads to certain peculiarities of behaviour which are discussed with the fluorides (p. 728). In iodine the electronegative character of the group is so far weakened that some tendency to electropositive behaviour appears. The halogens can attain the electronic configuration of the adjacent inert gas in two ways: first, by absorbing an electron to give the anion X′; secondly, by release of an electron, followed by co-ordination with a donor molecule, such as pyridine. The result is a cation, $(X \leftarrow py)^{\cdot}$. Fluorine excepted, all the halogens form salts of such cations, but those of iodine are the most numerous and the most stable. On electrolysis the iodine salts release iodine at the cathode. The amphoteric behaviour of hypoiodous acid (p. 751) is probably to be explained by assuming that water can to some extent act as donor to stabilize I˙ as $(I \leftarrow H_2O)^{\cdot}$. Among the inorganic compounds of terva-lent iodine are found a nitrate, $I(NO_3)_3$, a perchlorate, $I(ClO_4)_3.2H_2O$, and the oxide I_4O_9 may be written $I(IO_3)_3$. In these bodies the triposi-tive cation $I^{\cdots}$ may exist, but, at present, in the absence of know-ledge of their structures, such an assumption may be premature.

The hydrogen halides form an equally well-marked series. The

–	HF	HCl	HBr	HI
Melting-point	$-84°$	$-111°$	$-82°$	$-51°$
Boiling-point	$19°$	$-83°$	$-69°$	$-35°$
Heat of Formation of gas (calories)	64,270	22,130	8,690 (Br₂ liq.)	$-5,952$ (I₂ solid)

THE HYDROGEN HALIDES

abnormality of hydrogen fluoride will be noted, and is undoubtedly connected with the association of this substance. As might be

expected from the heats of formation, the dissociation into hydrogen and halogen in the gas phase requires a lower temperature with increasing atomic number of the halogen. The solubility of the gases in water, always very high, increases in this order.

The individuality of the elements comes out most strongly in their oxides. In the oxyacids of type $HClO_3$, formed by all the halogens with the exception of fluorine, the order of stability differs from that of the hydrogen halides, for iodine will displace bromine or chlorine from the bromates or chlorates, while bromine will displace chlorine, at least partially, from the chlorates. Chlorine and iodine are the only halogens to form acids of type $HClO_4$. Perchloric acid and its salts are remarkably stable in solution, while the several condensed forms of periodic acid are characteristic.

SEPARATION OF THE HALOGENS IN THEIR SALTS.—Fluorides can be removed without difficulty by precipitation of the other halides with silver nitrate, since silver fluoride is soluble. The other halides can be separated in solution by making use of the differences in the electrode potentials; they are usually liberated at a silver anode with a carefully regulated potential, and are weighed as silver halide. Alternatively chemical methods may be used, and the iodine alone liberated with a ferric solution; the oxidation potential $Fe^{...} \rightarrow Fe^{..}$ is $+0.77$ volt. From a mixed solution of chloride and bromide, bromine alone can be liberated by a permanganate solution of suitable acidity, but for this determination the conditions must be carefully watched. Alternatively the two halogens may be precipitated as silver halide, which is weighed and then heated in a stream of chlorine, to convert all the bromide to chloride. The weighing is then repeated.

FLUORINE

$F = 19.00.$ *Atomic Number*, 9

History.—Though hydrofluoric acid was obtained, in an impure state, by the action of concentrated sulphuric acid upon fluorspar or 'Blue John' (CaF_2), as early as 1771 (SCHEELE), it was not until 1810 that AMPÈRE suggested that it might be a compound of hydrogen with an unknown element, *fluorine*, analogous to chlorine. GAY-LUSSAC and THENARD had previously (1809) carried out a thorough investigation of the acid, which they believed to be an oxide of a new radical; but after DAVY (1810) had shown that chlorine is an element, the similarity between hydrochloric acid and hydrofluoric acid made it extremely probable that Ampère's

suggestion was correct. In spite of great ingenuity and perseverance, however, it proved impossible to isolate fluorine until 1886, when MOISSAN triumphed over severe experimental difficulties.

Occurrence.—Fluorine is a fairly abundant element, half as abundant, perhaps, as chlorine. The only important fluorine-containing minerals are *fluorspar*, calcium fluoride, CaF_2, and the less common *cryolite*, sodium fluoaluminate, Na_3AlF_6.

Preparation.—Fluorine is the most reactive of all elements, and its preparation caused extraordinary difficulty. To this day no chemical reaction, apart from electrolysis, is known from which useful quantities of fluorine are liberated, and the attempt to prepare it by the electrolysis of aqueous solutions always leads to the evolution of oxygen, whose electrode potential is far below that of fluorine. The problem was solved for the first time in 1886 by the French chemist Moissan, who succeeded in preparing fluorine by the electrolysis of potassium hydrogen fluoride, KHF_2, dissolved in anhydrous hydrogen fluoride in a platinum apparatus with platinum - iridium electrodes. The rapid modern development and utilization of fluorine compounds, especially of fluorinated hydrocarbons, has stimulated the large-scale production of fluorine.

FIG. 142. THE PREPARATION OF FLUORINE

The electrolyte, which is fluid at 100°, consists of a mixture of potassium hydrogen fluoride, KHF_2, with hydrogen fluoride, containing 40 per cent of the latter. The outer vessel of steel serves also as cathode, and 'monel metal' is used for the diaphragm. The anode is formed of graphite. Stoppers and other fittings may be made of 'Teflon,' a solid polymer of perfluoroethylene, $(C_2F_4)_n$. Arrangement is made for the addition of hydrogen fluoride as electrolysis proceeds. Hydrogen fluoride contaminating the crude gas is removed by passage through towers containing sodium fluoride, which is converted into $NaHF_2$. Fluorine is now safely compressed and transported in 'tanks' of nickel or 'monel metal.'

Properties.—Fluorine, F_2, is a greenish-yellow gas, lighter in colour than chlorine; it boils at −188° and freezes at −223°. It has an excessively pungent but otherwise not disagreeable smell, and instantly attacks animal tissue, producing severe wounds. It reacts with nearly all elements, often with incandescence, in

the cold, but not with oxygen, nitrogen, chlorine, or carbon (unless finely divided), though all forms of carbon unite with fluorine at a sufficiently high temperature. It vigorously attacks water, forming hydrogen fluoride and oxygen with a considerable proportion of ozone, and also attacks moist glass, but if the glass is perfectly dry to reaction takes place. Fluorine will displace oxygen, all the halogens, nitrogen, sulphur, or phosphorus from their binary compounds, such as the oxides or chlorides.

Hydrogen fluoride, $(HF)_n$.—Fluorine combines with hydrogen with great violence, even at temperatures at which both the elements are liquid, and hydrogen fluoride is also produced when fluorine acts on organic substances. It is most conveniently prepared by the distillation of a fluoride, usually calcium fluoride, with concentrated sulphuric acid in a lead or platinum apparatus, for the acid attacks glass. On the large scale the acid is distilled from cast-iron retorts, collected in water-cooled lead condensers, and preserved in bottles made of ceresine wax. By this method it is obtained as an aqueous solution containing fluosilicic acid (H_2SiF_6) as an impurity derived from silica in the calcium fluoride; this may be precipitated as the insoluble potassium salt by the addition of a little caustic potash, and the acid purified by another distillation.

The anhydrous compound is most easily prepared by heating potassium hydrogen fluoride, KHF_2, in a platinum apparatus and collecting the product in a freezing-mixture. Water is first removed from the salt by heating it for several hours to $150°$. Hydrogen fluoride is a colourless mobile liquid, boiling at $19°$ and freezing at $-84°$. It is an excessively dangerous substance. The concentrated or anhydrous acid produces dangerous wounds on the skin, and the inhalation of quite small quantities of the vapour in the course of laboratory experiments has led to permanent loss of voice and even to death.

There is every indication that hydrogen fluoride is associated. Not only is the boiling-point much higher than would be inferred from the boiling-points of the other hydrogen halides, but the vapour density near the boiling-point leads to a molecular weight of nearly four times the normal, decreasing to little above normal at, say, $60°$. These values were determined by weighing a large platinum vessel filled with the gas at various temperatures and pressures. The ionization of the solutions is of great interest, and is distinguished from that of the other hydrogen halides by the existence of complexes, as revealed by conductivity measurements, conductivity titrations, studies of chemical equilibrium, and other methods. Conductivity measurements in dilute solution show that the monomeric acid HF is comparatively weak, with a

2A

dissociation-constant of about 7×10^{-4} (25°). More concentrated solutions, however, contain considerable quantities of HF_2 ions, the equilibrium-constant $\dfrac{[HF] \, [F']}{[HF_2']}$ of the action

$$HF + F' \rightleftharpoons HF_2'$$
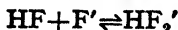
being 0·19. Aqueous solutions of the acid therefore contain chiefly undissociated molecules of HF, with some HF_2' and some F' ions, as well as some H˙ (see also p.367).

Though such salts as KHF_2 are known, hydrofluoric acid cannot properly be termed dibasic, as the normal fluoride, is not K_2F_2 but KF.

Hydrogen fluoride mixes with water in all proportions: distillation yields a constant-boiling mixture containing 36 per cent of the acid. It is a very active substance which attacks glass, forming silicon tetrafluoride:

$$SiO_2 + 4HF = SiF_4 \uparrow + 2H_2O,$$
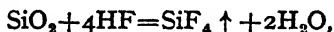
and is used for marking the graduations on glass apparatus or the letters on glass surfaces. The glass is covered with wax, which is scraped away where a mark is to be made, and is then exposed to the vapour for an opaque mark, or to the solution for a transparent one. The acid dissolves nearly all metals, gold and platinum being the principal exceptions. The remarkable solvent powers of this acid on metals are due less to its acid strength, which is indeed rather feeble, than to its great tendency to form complex fluorides with the metal in the anion. Its solvent action on silicates, often used in the treatment of silicate rocks for analysis, is due to the stability of the fluosilicate ion, SiF_6''.

FLUORIDES.—The fluorides may be prepared by the action of the acid on the metal, oxide, hydroxide, or carbonate, but some of the higher fluorides—e.g. sulphur hexafluoride—require elementary fluorine for their preparation, and a low temperature is sometimes necessary. Often the fluoride can be obtained from the chloride, either by distillation from a mixture with hydrogen fluoride, or with the help of silver fluoride, which readily forms silver chloride.

From a majority of elements fluorine evokes, in uncharged molecules or in anions, the highest known covalency. Fluorine is the most electronegative element, and quite often the fluoride of an element is an electrovalent compound while the other halides are largely covalent, e.g. aluminium, mercury (-ic). Consequently cations easily discharged from solution—e.g. those of silver or mercury (-ous)—often form soluble salts with fluorine as anion, when the other halides are insoluble. The most important covalent fluorides are those of boron, carbon, silicon, the halogens, and the

highest fluorides of the elements of Groups V and VI (except chromium). The fluorides of the other elements are for the most part salt-like in character, if they dissolve in water the solutions have an alkaline reaction from hydrolysis. Many of them are unchanged by heating in air or oxygen when the other halides are converted to oxides or oxyhalides. Most of the covalent fluorides are decomposed by water, but this does not happen if the covalency maximum has been reached; thus water decomposes silicon tetrafluoride but not carbon tetrafluoride; tellurium hexafluoride but not sulphur hexafluoride.

The ease with which elements display a high covalency in combination with fluorine leads to a large number of complex fluorides— e.g. BF_4', AlF_6''', SiF_6'', ZrF_7'''. Because the element other than fluorine attains maximum covalency, and fluorine is univalent, all fluo-acids, corresponding with such anions, are strong electrolytes, contrasting with the weakness of most oxy-acids.

Oxygen difluoride, Fluorine oxide, F_2O.—It was for many years supposed that no compound existed between oxygen and fluorine, but in 1927 fluorine oxide was prepared by the electrolysis of fluorides in presence of a little moisture. It is now always prepared by passing a fine stream of fluorine through dilute caustic soda:

$$2F_2 + H_2O = 2HF + F_2O \uparrow.$$
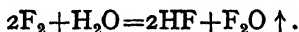
It is a colourless gas which at $-146°$ can be condensed to a yellow liquid freezing at $-224°$. It is a powerful oxidizing agent and will liberate the halogens from halide solutions, e.g.:

$$F_2O + 4I' + H_2O = 2I_2 + 2F' + 2OH'.$$
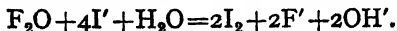
The gas is slowly decomposed by excess of alkali:

$$F_2O + 2OH' = 2F' + O_2 \uparrow + H_2O.$$
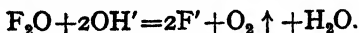
Another oxide of fluorine, F_2O_2, has been described.

FLUORIDES OF THE HALOGENS.—Chlorine and bromine form trifluorides, and iodine a pentafluoride and heptafluoride. **Chlorine monofluoride,** ClF, has also been described. It is a gas, boiling-point $-101°$, melting-point $-154°$.

Chlorine trifluoride, ClF_3, obtained by the action of excess of fluorine on chlorine, is a pale green liquid which boils at $11°$, forming a colourless gas, and freezes at $-83°$.

Bromine trifluoride, BrF_3, is prepared by the action of fluorine on bromine or potassium bromide:

$$KBr + 2F_2 = FK + BrF_3.$$
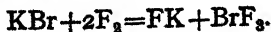
It is a yellow liquid, freezing at $9°$ and boiling at $127°$. The vapour

has an irritating smell, and the liquid fumes in air and attacks glass. It is almost as reactive as fluorine itself: it reacts violently with water and converts iodine with incandescence into iodine penta-fluoride, IF_5.

Iodine pentafluoride, IF_5.—This compound is produced when fluorine acts on iodine or an iodide, but was first prepared by GORE in 1875 by the action of iodine on silver fluoride in a platinum vessel:

$$5AgF + 3I_2 = IF_5 + 5AgI.$$
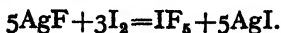
It is a heavy colourless fuming liquid, which freezes at —9·6° and boils at 97°. If strongly heated the vapour decomposes into its elements. Iodine pentafluoride is violently decomposed by water:

$$2IF_5 + 6H_2O = 2HIO_3 + 10HF,$$
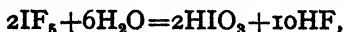
and is a highly reactive compound which slowly attacks even dry glass: with the elements it usually forms a fluoride and either iodine or an iodide.

Iodine heptafluoride, IF_7, is a colourless gas obtained by heating iodine pentafluoride with fluorine. On cooling colourless crystals are formed, which sublime at about 0°.

CHLORINE

$Cl = 35·457.$ *Atomic Number,* 17

History.—Chlorine was first isolated in 1774 by SCHEELE, who prepared it by the action of muriatic acid (HCl) upon pyrolusite (MnO_2). He regarded the action as a removal of phlogiston from the acid, and therefore named the new greenish, gaseous product *dephlogisticated muriatic acid air*. When the phlogiston theory was replaced by the oxygen theory of LAVOISIER, chlorine was con-sidered to be a compound of oxygen and muriatic acid; hence it was called *oxymuriatic acid*. In 1810, Davy found it impossible to extract oxygen from oxymuriatic acid by any of the numerous means that suggested themselves to him, and for this reason concluded that it was an element. After consultation with other chemists, he proposed to call it *chlorine*, from the Greek χλωρός, *chloros*, greenish-yellow

Occurrence and Man———.—Chlorine is an abundant element —the most abundant of the halogens. Most of the chlorine of commerce is made from sodium chloride. Many attempts have been made to manufacture chlorine from the calcium chloride which is produced in such large quantities as the residue of manufacturing processes (p. 442), but these have not, for the

most part, been commercially successful. On the commercial scale chlorine is made either by the electrolysis of brine, or by the oxidation of hydrogen chloride, itself manufactured from salt. The former method has already been described under the heading of caustic soda (p. 437).

During the war of 1939–45, when heavy demands were made on the production of chlorine as well as on that of electric power, non-electrolytic methods for the manufacture of chlorine, such as the Deacon process, were revived.

The DEACON process is carried out in the gas phase on the surface of a catalyst, the oxidizing agent being air:

$$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2.$$
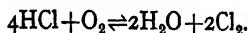
The oxidation takes place with the evolution of heat, and is therefore more nearly complete at low temperatures than at high ones, provided that equilibrium is reached. But at low temperatures the action is very slow, even on the surface of the best available catalysts, and consequently an intermediate temperature is used corresponding with only partial conversion. By using oxygen instead of air, or by increasing the pressure, better yields could be obtained, but these expedients have not up to the present been found remunerative. The catalyst is cupric chloride, and the temperature used is about 440°, at which the percentage of hydrogen chloride actually oxidized is about 65 per cent. As in all similar operations, the reaction mixture must be carefully purified, or the catalyst will be poisoned; this is accomplished by washing the gas with sulphuric acid and passing it through dust-collecting plant. After pre-heating to about 220°, the gas enters the contact chambers, which are filled with earthenware balls soaked in a concentrated solution of cupric chloride and dried. On leaving the contact chambers the mixed gases meet sprays of water, which wash out any unchanged hydrogen chloride, and then contain not more than 12 per cent of chlorine by volume. This dilute chlorine is, however, sufficiently concentrated for the manufacture of bleaching powder (for which it is usually required) in suitable plant. The successive reactions on the catalyst are considered to be as follows:

(1) $2CuCl_2 = 2CuCl + Cl_2$,   (2) $4CuCl + O_2 = 2Cu_2OCl_2$,
(3) $Cu_2OCl_2 + 2HCl = 2CuCl + H_2O + Cl_2$.
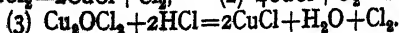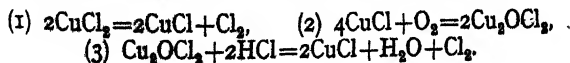
Chlorine is usually transported in the liquid state, and liquid chlorine is now a common article of commerce. The gas for this purpose must be concentrated (Deacon chlorine is unsuitable); it is dried with concentrated sulphuric acid and liquefied by compression to six atmospheres. The liquid can safely be carried in steel cylinders or tank-cars if it is dry.

The principal use of chlorine is in the manufacture of bleaching powder (p. 496) and hydrochloric acid; it is also used in the manufacture of synthetic dyes and in sterilizing water supplies. In the war of 1914–18 it was the first poison gas to be used. In the laboratory it is used as an oxidizing or chlorinating agent, and may be prepared for this purpose by the oxidation of concentrated hydrochloric acid. This substance may be heated with manganese dioxide:

$$4HCl + MnO_2 = Mn^{\cdot\cdot} + 2Cl' + Cl_2 \uparrow + 2H_2O,$$
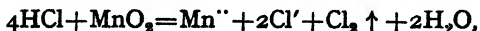
or simply dropped on to solid potassium permanganate:

$$16HCl + 2MnO_4' = 2Mn^{\cdot\cdot} + 6Cl' + 5Cl_2 \uparrow + 8H_2O.$$
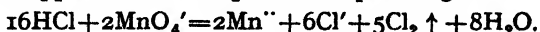
Chlorine from these sources may contain traces of oxygen, and if gas of the highest purity is required—as for instance for atomic weight work—it should be prepared by heating the chlorides of gold or platinum in a vacuum, or by the electrolysis of pure fused silver chloride. The gas may be dried with concentrated sulphuric acid.

Properties of Chlorine.—Chlorine is a greenish-yellow gas with a suffocating smell, and is more than twice as dense as air. The inhalation of chlorine diluted with air has been recommended as a cure for catarrh. Chlorine can be liquefied without difficulty at room temperature by compressing it to some six atmospheres. It is not very soluble in water: at 15° and atmospheric pressure a saturated aqueous solution contains about 8 gm. of chlorine per litre. By cooling such solutions to a low temperature crystals of *chlorine hydrate* are obtained, the formula of which has been variously given as $Cl_2.7H_2O$, $Cl_2.8H_2O$, and $Cl_2.10H_2O$. These crystals decompose when allowed to regain room temperature.

Chlorine is a highly reactive substance which combines with most metals to form chlorides, often with incandescence (e.g. antimony or aluminium). Among other metals, platinum, gold, and mercury are all attacked. It combines with hydrogen in the light (p. 273), but mixtures of the two gases can be kept indefinitely in the dark. A jet of chlorine will burn in hydrogen and vice versa. The affinity of chlorine for oxygen, on the other hand, is slight, and direct combination cannot be effected.

Chlorine Water.—Solutions of chlorine in water have the properties of hydrochloric and hypochlorous acids, produced as follows:

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO.$$

The equilibrium was investigated by JAKOWKIN by two methods:

    (i) The concentration of the acids can be determined by conductivity methods, since it is reasonable to suppose that molecules of chlorine do not conduct the current.

(ii) The partition of chlorine can be measured between water and carbon tetrachloride, a liquid which extracts only negligible concentrations of hydrochloric or hypochlorous acids from aqueous solution. The hydrolysis causes variation in the partition-ratio, and the degree of hydrolysis can be calculated from the observed ratio. A solution containing about 4 gm. per litre at 0° is about 30 per cent hydrolysed: the degree of hydrolysis increases with the temperature. The hydrolysis is entirely reversible, and if the solution is made strongly acid, chlorine is evolved.

The least volatile constituent of chlorine water is the hydrochloric acid, and this substance alone remains behind as a dilute solution when chlorine water is boiled for some time. If exposed to light, chlorine water is also unstable at lower temperatures, and evolves oxygen:

$$2Cl_2 + 2H_2O = O_2 \uparrow + 4HCl,$$
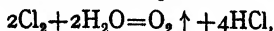
but if the solution is concentrated, some chloric acid may also be produced by decomposition of the unstable substance hypochlorous acid:

$$8HClO = 2HClO_3 + 6HCl + O_2 \uparrow.$$
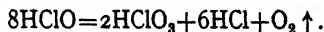
The bleaching powers of moist chlorine are due to the hypochlorous acid which it produces in contact with water. Many coloured substances, such as indigo, can be converted by moist chlorine to colourless oxidation-products. The oxidizing power of chlorine is a necessary consequence of its affinity for hydrogen; thus it will oxidize gaseous ammonia to nitrogen:

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl.$$
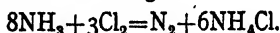
The reaction is accompanied by a vivid red flash, easily visible if it is carried out in the dark. If, however, the reaction is carried out in warm aqueous solution and the chlorine is in excess, the product is chiefly nitrogen trichloride (p. 423):

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl.$$
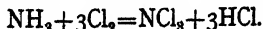
Chlorine will also combine with several oxides to form oxychlorides —e.g. with nitric oxide or sulphur dioxide. The oxidizing powers of chlorine are frequently used in the laboratory, as for the conversion of ferrous to ferric salts or thallous to thallic, and the solvent action of aqua regia on gold is partly due to the chlorine which it contains. Chlorine will react with many organic substances, particularly those rich in hydrogen, liberating hydrogen chloride; warm turpentine, for instance, will catch fire if placed in the gas, burning with a red flame and emitting clouds of carbon.

Hydrogen chloride, HCl.—This substance is manufactured on a very large scale in the salt-cake processes already described (p. 451). Nowadays, however, it is also often produced by the

combustion of chlorine in an atmosphere of hydrogen. Both these gases are by-products of the electrolysis of brine for the manufacture of caustic soda (p. 437), and the choice of method is chiefly controlled by the cost of electric power in the neighbourhood. The net result of the electrolysis of brine is then:

$$NaCl + H_2O = NaOH + HCl,$$

the exact reverse of the neutralization of an acid by a base. The gas is always absorbed in water, in which it is extremely soluble, and is sold in large glass carboys; the concentrated acid of commerce contains about 1 part of hydrogen chloride in 2 parts of water by weight. The principal industrial use of hydrochloric acid is for the preparation of chlorine; in the laboratory it is used for this and many other purposes.

Crude commercial acid contains ferric chloride, from iron containers, which gives it a yellow colour, and may also contain sulphur dioxide, sulphuric acid, and arsenic chloride. Electrolytic acid is, however, very pure. It may be boiled with a little permanganate, to expel any bromine or iodine, and once distilled, only the middle portion being retained; it is then sufficiently pure for all purposes. In the laboratory pure hydrogen chloride can be prepared by dropping concentrated sulphuric acid on to pure concentrated hydrochloric acid: the heat developed from the sulphuric acid and water is sufficient to expel a steady stream of the gas, which should be dried with concentrated sulphuric acid. The direct combination of hydrogen and chlorine has already been discussed (p. 273).

FIG. 143. THE FOUNTAIN EXPERIMENT.

Hydrogen chloride is a colourless gas with a very pungent taste and smell; it is rather denser than air. It is exceedingly soluble in water, as is sometimes demonstrated with the help of the well-known ' fountain ' experiment. The flask, fitted as in the diagram, is filled with the gas and inverted over water in which the straight tube is immersed. When the tap is opened, the gas in the flask dissolves and water rushes up the tube until nearly the whole of the flask is full. Suction on the side-tube may be necessary to start the flow, but once water has entered the flask nearly all the gas dissolves in it, and the resulting reduction of pressure causes the flask to fill.

At 25°, 100 gm. of a solution saturated with hydrogen chloride at atmospheric pressure contain about 41 gm. of hydrogen chloride. The addition of either water to hydrogen chloride or vice versa lowers the vapour pressure, and the solution with the lowest vapour pressure—and therefore the highest boiling-point—contains 20·24 per cent hydrogen chloride. When solutions of hydrogen chloride are distilled, this constant-boiling solution therefore remains in the retort, a fact made use of in the preparation of solutions of standard acidity (p. 170). This solution boils at 110°.

If concentrated hydrochloric acid is confined, as in the diagram, in an atmosphere saturated with water-vapour, the hydrogen chloride leaving the acid forms, with the water-vapour in the air, a dilute acid with a vapour pressure lower than that of either the concentrated acid or water. This acid therefore condenses in fumes, and this happens whenever the concentrated acid is exposed to moist air.
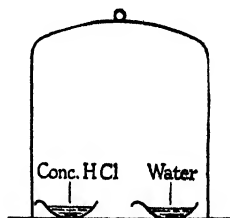
FIG. 144. THE FUMING OF HYDROCHLORIC ACID

Three *hydrates of hydrogen chloride* are known. They have the formulae $HCl.H_2O$, $HCl.2H_2O$, and $HCl.3H_2O$, and can be obtained as colourless crystals by cooling solutions of suitable concentration. Solutions of hydrogen chloride do not even approximately obey HENRY's law. The partial pressure of the gas over its dilute solutions is exceedingly small, and at a concentration of five times molar is only a quarter of a millimetre of mercury (25°), so that dilute solutions of hydrogen chloride can be boiled without appreciable loss of acid. In very concentrated solutions the partial pressure increases very rapidly with the concentration. The existence of any partial pressure of hydrogen chloride molecules over its dilute aqueous solutions shows that the dissociation of the acid cannot be *absolutely* complete, since some undissociated molecules must be present in the liquid phase to maintain the distribution-ratio; but the minuteness of the pressure shows this proportion to be exceedingly small. Similar conclusions are reached as the result of distribution measurements on hydrogen chloride between water and solvents, such as benzene or nitrobenzene, in which it is freely soluble but from which it is almost wholly extracted by water (p. 184). In these solvents, as in air, hydrogen chloride is undissociated; in a well-known lecture experiment it is shown that a solution of dry hydrogen chloride in dry toluene will neither decompose marble nor produce a precipitate with a toluene solution of silver nitrate. The presence of a hydroxyl group in the solvent appears to be necessary for the ionization of this compound. Its

solutions in the lower alcohols at least are fully ionized, as is shown by conductivity measurements.

An examination of the properties of pure hydrogen chloride leaves no doubt that it is a covalent compound. The pure liquid is very volatile (boiling-point $-83°$), and conducts electricity no better than pure water; it dissolves in indifferent solvents such as benzene, and these solutions are not ionized. When dissolved in water hydrogen chloride shows a remarkable change in properties and becomes an acid. The anhydrous substance has none of the properties of an acid and this term should be rigorously reserved for its solutions in water. There can be little doubt that the true reason of the change is the solvation of the ions, and probably the co-ordination of the hydrogen ion with water or hydroxyl-containing molecules:

$$HCl + (m+n)H_2O \rightleftharpoons H^{\cdot}.nH_2O + Cl'.mH_2O.$$

This chemical effect is considered to be more important than the purely electrical effect, partly on account of the experiments on alcoholic solutions already described (p. 158), and partly because nitrobenzene does not ionize hydrogen chloride, although possessed of a higher dielectric constant than ethyl alcohol, which does.

Hydrogen chloride can be oxidized to chlorine by oxygen at a moderate temperature and in the presence of a catalyst. At room temperature the action:

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O,$$
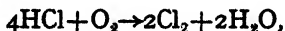
has a positive affinity, but takes place extremely slowly, If, however, a mixture of moist hydrogen chloride and oxygen is exposed to light it is possible to detect a trace of chlorine in the mixture. Even when a catalyst is used it is, however, necessary to use a much higher temperature to secure a reasonable reaction velocity. Hydrogen chloride reacts with many of the metals, either in the cold or on heating, producing hydrogen and the chloride of the metal. If the metal has more than one chloride, the lowest is naturally produced:

$$Fe + 2HCl \rightleftharpoons FeCl_2 + H_2.$$

Chlorides.—Chlorides may be prepared in solution:

(i) By the action of hydrochloric acid on a metal, or on the oxide, hydroxide, or carbonate.

(ii) By direct combination: this usually produces the highest chloride if the chlorine is in excess.

(iii) By the action of hydrogen chloride on the element: this usually produces a lower chloride, if there is one.

(iv) By acting on the oxide or sulphide with chlorine, sulphur

chloride, or carbon tetrachloride. It is sometimes necessary to mix the oxide with carbon, and it must nearly always be heated. This method can be used only for chlorides volatile at the temperature of the experiment.

(v) Chlorides can also be made by acting on bromides or iodides, either in the dry state or in solution, with chlorine.

Chlorides may be either covalent or electrovalent, the first class corresponding with the non-metals and the second with the metals, but there are many compounds of intermediate type and the classification is not rigid. The electrovalent chlorides are usually colourless solids soluble in water, but silver, lead, mercurous, cuprous, aurous, and thallous chlorides are insoluble or slightly soluble: many of these are the chlorides of metals easily precipitated as metal from solutions of their salts.

The covalent chlorides are nearly all decomposed by water, though carbon tetrachloride is an exception (p. 578). It has been pointed out by Sidgwick that hydrolysis of chlorides can take place in two ways, according to whether the water acts as donor or acceptor. In the first the products are hydrochloric acid and a hydroxide; this is shown by the chloride of such an acceptor element as boron:

$$BCl_3 + H_2O \qquad Cl-B\leftarrow O \qquad \rightarrow 3HCl + B(OH)_3$$
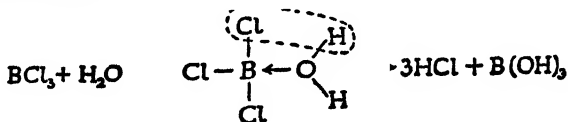
With the chloride of a donor element such as nitrogen, however, hypochlorous acid may be formed:

$$NCl_3 + H_2O \cdot \quad Cl-N\rightarrow H\cdot O-H \quad \cdot 3HClO + NH_3 \text{ Etc.}$$
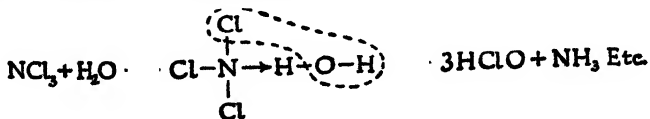
OXIDES OF CHLORINE.—The oxides of chlorine include the monoxide Cl_2O, the dioxide ClO_2, and the heptoxide Cl_2O_7.

Chlorine monoxide, Cl_2O.—This compound is produced by the gentle oxidation of chlorine with mercuric oxide. The reaction is carried out at room temperature, and the mercuric oxide must be prepared by precipitation and ignition. The chlorine monoxide is removed from the gas stream which leaves the reaction vessel by passage through a freezing-mixture at $-20°$. The other product is a yellowish-brown oxychloride of mercury:

$$2HgO + 2Cl_2 = Hg_2OCl_2 + Cl_2O.$$
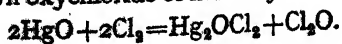
Chlorine monoxide is a heavy gas with a colour and smell somewhat resembling those of chlorine. It can be condensed to a brown liquid boiling at 2°. It is very soluble in water, with which it forms hypochlorous acid, and is, in fact, hypochlorous anhydride:

$$Cl_2O + H_2O = 2HClO.$$

It is an unstable substance which may decompose spontaneously, and oxidizes many substances, such as paper or phosphorus, with inflammation and sometimes with explosion. Chlorine monoxide differs from chlorine in its much greater solubility in water and in not reacting with mercury, over which it can be collected.

Chlorine dioxide, ClO_2.—This dangerous compound is evolved when a cold mixture of potassium chlorate and concentrated sulphuric acid is gently warmed to 30°–40°:

$$3HClO_3 = HClO_4 + H_2O + 2ClO_2 \uparrow.$$

The sulphuric acid may with advantage be replaced by crystallized oxalic acid and a little water; this method is safer. The product contains some carbon dioxide, but this can be removed by condensing the chlorine dioxide in a freezing-mixture.

Chlorine dioxide is a heavy orange gas, with a peculiar smell, which can be condensed to a liquid at 11°. It is freely soluble in water. The gas is highly explosive, particularly in the presence of oxidizable substances, so cork, rubber, or paper even in the smallest quantities must be avoided in its preparation. The gas or its solutions are stable in the dark, but if exposed to sunlight the gas may detonate for no apparent reason, and the solution decomposes with the formation of chlorine, oxygen, chloric and perchloric acids. Chlorine dioxide is a powerful oxidizing and bleaching agent, and, diluted with air to 'safe' proportions, is used in treating flour, in place of the harmful 'agene,' NCl_3, formerly so employed.

Chlorine heptoxide, Cl_2O_7.—This substance is perchloric anhydride. It was first made (1900) by distillation of a mixture of anhydrous perchloric acid and phosphorus pentoxide which had stood for a day in a freezing-mixture:

$$2HClO_4 - H_2O = Cl_2O_7.$$
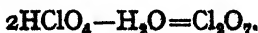
It is a colourless volatile liquid, boiling at 82°, which slowly decomposes. Its preparation is sometimes attended by violent detonations. When mixed with water it forms perchloric acid, but the reaction is quiet.

OXYACIDS OF CHLORINE AND THEIR SALTS.—The oxyacids of chlorine are *hypochlorous acid*, $HClO$; *chlorous acid*, $HClO_2$; *chloric acid*, $HClO_3$; and *perchloric acid*, $HClO_4$.

Hypochlorous acid, $HClO$, exists only in aqueous solution. Such solutions are prepared by leading chlorine monoxide into water,

or, more simply, by generating it from chlorine and mercuric oxide in a flask containing a little water. It can also be prepared by mixing a weak, non-volatile acid, such as boric acid, with excess of bleaching powder and distilling off the hypochlorous acid, mixed with water, under reduced pressure; or by passing chlorine into a cold carbonate solution and distilling as before:

$$Cl_2 + H_2O + CO_3'' = HClO + HCO_3' + Cl'.$$
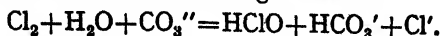
The two last methods of preparation depend on the very feeble acidity of the substance, which allows it to be distilled from only faintly acid solutions at low temperatures.

Solutions of hypochlorous acid are pale yellow and smell of chlorine monoxide, though the proportion of the gas present at equilibrium is very small. They decompose slowly in the dark and rapidly in the light, the principal products being hydrochloric acid and oxygen. With most oxidizing agents, mutual reduction takes place and oxygen is liberated: thus with hydrogen peroxide:

$$H_2O_2 + HClO = HCl + H_2O + O_2 \uparrow.$$
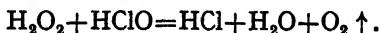
Hypochlorous acid is a powerful oxidizing agent which will liberate nitrogen from ammonium salts:

$$2NH_4' + 3HClO = 3HCl + 2H' + 3H_2O + N_2 \uparrow.$$

When mixed with hydrochloric acid and warmed, it liberates twice as much chlorine as it itself contains:

$$HClO + HCl = Cl_2 \uparrow + H_2O.$$
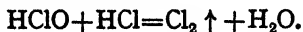
Hypochlorites.—When chlorine is passed into cold caustic alkali, a mixture of chloride and hypochlorite is produced:

$$Cl_2 + 2OH' = Cl' + ClO' + H_2O.$$
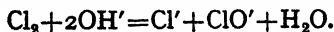
If caustic soda is used, most of the sodium chloride separates out, and in this way concentrated solutions of sodium hypochlorite in caustic soda can be obtained from which crystals of hydrated sodium hypochlorite, probably $NaClO.7H_2O$, are precipitated at low temperatures. Hypochlorite solutions are fairly stable in the dark, particularly if alkaline, but if heated they decompose into chloride and chlorate (see further, p. 740):

$$3ClO' = ClO_3' + 2Cl'.$$

The preparation and properties of bleaching powder have already been described (p. 496). Large quantities of hypochlorite solutions for bleaching purposes are now made by electrolysing brine, and this has injured the bleaching-powder industry.

Chlorous acid, $HClO_2$, and the Chlorites.—Chlorous acid is the least stable of the oxyacids of chlorine, and can be prepared only

with difficulty even in dilute aqueous solution, though the chlorites are comparatively stable. *Barium chlorite*, $Ba(ClO_2)_2$, can be made by passing chlorine dioxide into suspensions of barium dioxide:

$$2ClO_2 + BaO_2 = Ba(ClO_2)_2 + O_2 \uparrow.$$
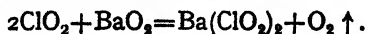
By treating this substance with dilute sulphuric acid it is possible to obtain a solution of chlorous acid. It is a powerful oxidizing agent, like hypochlorous acid, but unlike that substance is a strong acid. Solutions of the chlorites are not hydrolysed, and possibly owe their stability as compared with the hypochlorites to this circumstance, as both of the acids are highly unstable. The chlorites can be obtained from solutions of chlorous acid or barium chlorite: they are usually colourless substances soluble in water. On heating they readily decompose into chlorate and chloride:

$$3ClO_2' = 2ClO_3' + Cl'.$$
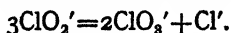
Chloric acid, $HClO_3$, and the Chlorates.—Chlorate solutions are prepared by the action of chlorine on *hot* alkaline solutions:

$$3Cl_2 + 6OH' = ClO_3' + 5Cl' + 3H_2O.$$

In spite of the chloride produced at the same time, the whole oxidizing power of the chlorine is preserved in the chlorate. This process is worked on a large scale, according to two methods; in one chlorine is led into hot milk of lime, and in the other hot chloride solutions are electrolysed without a diaphragm.

The product of the first process is neutralized, mixed with excess of potassium chloride, and artificially cooled to a low temperature, when a mixture of potassium chloride and chlorate is precipitated. Nearly pure potassium chlorate is obtained from it by recrystallization, since the solubility of this substance rises very steeply with the temperature.

The preparation of chlorate by the electrolysis of brine requires careful regulation of the conditions. If a diaphragm is used, the products are chlorine at the anode, and hydrogen and caustic soda at the cathode. If, however, the anode and cathode liquids are mixed, the chlorine is not given off, but is absorbed by the hydroxide with the formation of hypochlorite. At about 60° and in conditions of carefully controlled slight acidity, when both the weak hypochlorous acid and its anion co-exist, chlorate is rapidly formed by the successive reactions:

$$HClO + ClO' = ClO_2' + H^{\cdot} + Cl',$$
$$HClO + ClO_2' = ClO_3' + H^{\cdot} + Cl'.$$
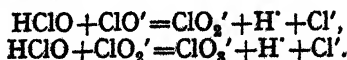
Loss of hypochlorite by reduction at the cathode is prevented by the presence of a small amount of chromate, from which by reduction a protective film is formed on the electrode.

Sodium or potassium chlorate is used in the manufacture of matches and explosives and as an oxidizing agent in the preparation of dyestuffs and other organic compounds.

Solutions of chloric acid are obtained by precipitating well-cooled solutions of barium chlorate with sulphuric acid and filtering. The acid cannot be prepared in the pure state, and decomposes, if the solutions are concentrated beyond a certain point, into chlorine, oxygen, perchloric acid, and other substances. Chlorates are usually obtained from potassium chlorate or by double decomposition from barium chlorate or silver chlorate, all of these substances being soluble in water. Chloric acid solutions are yellowish in colour and smell something like nitric acid. They slowly decompose on keeping, though if all impurities are absent the solutions are stable. Chloric acid is a strong electrolyte, and chlorate solutions show no signs of hydrolysis.

When chlorates are strongly heated the final residue is usually a chloride, e.g.:

$$2KClO_3 = 2KCl + 3O_2 \uparrow,$$
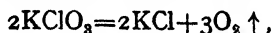
a reaction used in the common laboratory preparation of oxygen, but certain chlorates, such as those of magnesium and aluminium, lose chlorine and oxygen on heating and yield an oxide:

$$2Mg(ClO_3)_2 = 2MgO + 2Cl_2 \uparrow + 5O_2 \uparrow.$$
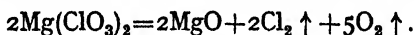
An intermediate stage in decompositions of the first kind is the formation of perchlorates, which are stabler than chlorates. The chlorates and chloric acid are fairly powerful oxidizing agents which are decomposed when heated with concentrated hydrochloric acid furnishing some chlorine dioxide in addition to the chlorine shown in the equation:

$$ClO_3' + 5Cl' + 6H^{\cdot} = 3Cl_2 \uparrow + 3H_2O.$$
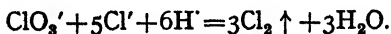
The oxidizing power of solid chlorates is still more apparent, and a mixture of potassium chlorate with sulphur, phosphorus, sugar or any other easily oxidizable substance is liable to explode. Dilute solutions of potassium chlorate are used as disinfectants, especially for gargling. The preparation and properties of this substance have already been described (p. 448).

Perchloric acid, HClO₄, and the Perchlorates.—The first stage in the decomposition of sodium or potassium chlorate by heat is the formation of a perchlorate, which then decomposes into a chloride and oxygen:

$$4NaClO_3 = 3NaClO_4 + NaCl \quad \text{and} \quad NaClO_4 = NaCl + 2O_2 \uparrow.$$
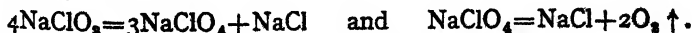
Perchlorate solutions can be prepared by the oxidation of chlorate solutions, though very powerful oxidizing agents, such as persulphates, are required for the purpose. The oxidation is therefore

most readily carried out electrolytically, and this is accomplished on the manufacturing scale. The starting-point is a concentrated solution of sodium chlorate, which is electrolysed at a temperature below 10° with iron cathodes and platinum anodes (high oxygen over-voltage). The energy efficiency is 85 per cent, and the process is carried nearly to completion, when the solution is mixed with potassium chloride, which precipitates the nearly insoluble potassium perchlorate (p. 449). It is used in explosives, as it is safer than potassium chlorate and contains more oxygen.

Aqueous solutions of perchloric acid can be prepared from barium perchlorate and sulphuric acid or from sodium perchlorate and concentrated hydrochloric acid, in which sodium chloride is only slightly soluble. Almost the whole of the hydrochloric acid can be expelled by heating the filtrate nearly to boiling. The anhydrous acid is prepared by distilling a mixture of potassium perchlorate and concentrated sulphuric acid under reduced pressure. The product contains some hydrogen chloride and chlorine dioxide, which can be expelled by blowing air through it. It is a colourless volatile liquid which fumes in moist air and decomposes on heating, though it can be distilled under reduced pressure at about 20°. The freezing-point is −112°. The liquid cannot exist at its boiling-point, but the constant-boiling mixture with water, which contains 72 per cent perchloric acid and can be distilled unchanged, boils at 203°. Anhydrous perchloric acid is a dangerous substance which burns the skin, violently oxidizes most organic substances, and is liable to spontaneous explosion.

Aqueous solutions of the acid, on the contrary, are not only perfectly safe but can be kept indefinitely without change in composition. The strongest solution supplied to the laboratory contains 60 per cent of the acid. Several solid hydrates of perchloric acid can be obtained by cooling solutions of suitable concentration. Perchloric acid is the most stable of all the oxyacids of chlorine, and is a powerful oxidizing agent only when in concentrated solution or anhydrous, whereas hypochlorous and chloric acids are too unstable to exist in the absence of water. Metals liberate hydrogen from dilute solutions of the acid, and these solutions have no bleaching power, nor will perchloric acid oxidize hydrochloric acid. It will however oxidize titanous solutions, and perchlorate solutions can be estimated volumetrically with the help of this reagent. A zinc-copper couple will reduce chlorate solutions to chlorides while leaving perchlorates unaffected: this is used in analysis.

Perchloric acid is not only fully dissociated in aqueous solution, but appears to preserve its ionization in non-aqueous solvents better than any acid hitherto investigated, and may be called the strongest of known acids. In ether, hydrogen perchlorate is about

.a hundred times as much dissociated as hydrogen chloride, and perchlorates are often more definitely electrovalent than the chlorides of the same metal. Thus aluminium perchlorate can be obtained by evaporation of its aqueous solutions, a process which hydrolyses aluminium chloride, and a further example is afforded by the corresponding compounds of mercury (p. 513). The perchlorate ion is very slightly solvated in hydroxylic solvents, for its mobility in water is higher than that of the chloride or chlorate ions, while in methyl alcohol it moves faster than any ion yet examined with the single exception of the hydrogen ion.

The *perchlorates* are usually colourless compounds soluble in water, but the perchlorates of potassium, caesium, and rubidium are nearly insoluble in cold water, though fully soluble in hot water. As sodium perchlorate is highly soluble at all temperatures, the recrystallization of potassium perchlorate provides an excellent method for preparing potassium compounds free from sodium. This salt is also widely used in the gravimetric estimation of potassium salts. At 10° a litre of a saturated solution of potassium perchlorate contains about 11 gm., but this quantity can be much reduced by the addition of alcohol to the solution. Like all perchlorates, the potassium salt on strong heating decomposes into a chloride and oxygen.

BROMINE

Br=79·916. *Atomic Number*, 35

History.—Upon passing chlorine through 'bittern' (i.e. the mother-liquor left after the recrystallization of salt from sea-water), BALARD (1826) noticed the formation of a brownish-yellow coloration. By evaporating the bittern to dryness, and heating the residue with manganese dioxide and concentrated sulphuric acid, he was able to collect a dark reddish-brown liquid with a powerful and pungent smell. This liquid was recognized to be an analogue of fluorine, chlorine, and iodine, and was called *bromine* (Greek βρῶμος, *bromos*, a stench).

By an unlucky chance, LIEBIG had failed to pay much attention to a specimen of a dark red liquid sent to him from a salt factory in Germany in 1820. Believing it to be merely iodine chloride, he missed his opportunity of discovering an important new element; for the liquid was bromine.

Occurrence and Manufacture.—Though very much less common than chlorine, bromine is a comparatively abundant element which occurs in combination with the alkali- and alkaline-earth metals in sea-water, in mineral deposits and in certain spring waters.

Most of the bromine of commerce is prepared from the liquors remaining after the crystallization of potassium chloride from carnallite, though some is prepared in America from Ohio springs. An electrolytic method is now in use. The electrolysis is carried out in diaphragm cells and the bromine collects in the liquid of the anode compartment. The difference between the standard electrode potentials of chlorine and bromine is 0·29 volt, which allows nearly all the bromine to be liberated first from a chloride-bromide solution. The bromine is recovered by boiling the solution and is collected in water-cooled condensers.

In the older process the bromine was expelled by passing chlorine from a cylinder through the bromide solution while it trickled through a tower filled with glass balls or provided with plates and bubblers. Any chlorine or bromine remaining in the liquid after this treatment was expelled with steam and recovered. The bromine was condensed by passing the vapours through a water-cooled coil, and chlorine, together with any uncondensed bromine, was then absorbed by moist iron filings.

In America, bromine is extracted from sea-water, which contains about 0·007 per cent of the element in the form of the bromine ion, Br'. On passing chlorine into sea-water, the bromine is liberated:

$$Cl_2 + 2Br' = 2Cl' + Br_2.$$
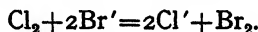
Sea-water is, however, slightly alkaline (pH=7·2), hence much of the bromine is hydrolysed to bromate (or hypobromite) and bromide:

$$3Br_2 + 3H_2O \rightleftharpoons 6H^{\cdot} + 5Br' + BrO_3';$$
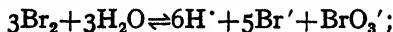
and since chlorine will not displace bromine from a bromate or hypobromite, considerable loss of bromine results.

By adding sufficient sulphuric acid to the sea-water (about 1 lb. of acid to 4 tons of water), the pH can be lowered to 3·5, and at this value the hydrolysis of the bromine is negligible.

The acidified sea-water, after treatment with chlorine, trickles down towers up which a current of air passes. This blows out the bromine as vapour, and carries it on to further towers in which it is removed by sodium carbonate solution:

$$3Br_2 + 3CO_3'' = 5Br' + BrO_3' + 3CO_2.$$

The solution of sodium bromide and bromate is treated with sulphuric acid to liberate the bromine, which vaporizes on heating and is condensed and collected.

The bromine prepared by these methods contains chlorine, from which it is freed at the factory by the addition of ferrous bromide followed by distillation. If perfectly pure bromine is required, the commercial product should be washed with water, dissolved in

a concentrated solution of potassium bromide, precipitated by dilution with water, separated, dried with quicklime followed by phosphorus pentoxide, and distilled in a current of carbon dioxide.

In the laboratory bromine may be prepared by heating bromides with manganese dioxide and sulphuric acid. The preparation of exactly measured quantities of bromine for analytical work is most accurately accomplished by the addition of acids to standard bromate solutions in the presence of excess of bromide:

$$BrO_3' + 5Br' + 6H^{\cdot} = 3Br_2 + 3H_2O.$$

Bromine is used in the synthesis of dyestuffs and other organic compounds and in the preparation of anti-knock petrol. In the laboratory it is used in analysis and as a mild oxidizing agent.

Properties.—Bromine is a dense liquid (density 3·2), in colour dark red-brown, and with a very pungent suffocating odour: it is one of the few elements liquid at room temperature. It boils at 59°, emitting a heavy red-brown vapour, and freezes at —7°. The vapour has the normal molecular weight, and even at 1000° the dissociation into bromine atoms amounts to only 4 per cent.

Bromine is not very soluble in water: a litre of a solution saturated at room temperature contains about 37 gm. of the element. At low temperatures red crystals of bromine hydrate, $Br_2.10H_2O$ or perhaps $8H_2O$, may be obtained. The solutions have a slightly acid reaction from hydrolysis, but this is much less noticeable than with chlorine water. Bromine dissolves much more readily in such solvents as chloroform or carbon tetrachloride than in water, and can be extracted from its aqueous solutions by these solvents. The solutions are very dark in colour. It is also readily soluble in bromide, and to a less degree in chloride, solutions, forming complex ions $ClBr_2'$ and Br_3'. Bromine is much less active than chlorine, but combines directly with several elements such as potassium or aluminium. Hydrogen and bromine can be mixed without reaction in the brightest sunlight (p. 273), but react when heated.

Hydrogen bromide, HBr.—Since this compound, like hydrogen iodide, is easily oxidized by hot concentrated sulphuric acid, it cannot conveniently be prepared by the action of this substance on a bromide. It is prepared by the hydrolysis of phosphorus tribromide:

$$PBr_3 + 3H_2O = 3HBr \uparrow + HPO(OH)_2.$$

In practice, bromine is dropped on to a mixture of red phosphorus and water. The reaction takes place, with a slight luminescence, in the cold, and the gas evolved is passed over moist red phosphorus

to free it from bromine, and collected over mercury. It can also be prepared by the action of bromine on cold benzene containing a little aluminium powder as halogen carrier:

$$Br_2 + C_6H_6 = HBr \uparrow + C_6H_5.Br.$$

A more convenient method of preparing hydrogen bromide is to heat potassium bromide with syrupy phosphoric acid:

$$KBr + H_3PO_4 = KH_2PO_4 + HBr \uparrow .$$

The gas obtained by these methods may be dried with anhydrous calcium bromide. It is a heavy colourless gas, freezing at $-82°$ and boiling at $-67°$, and is exceedingly soluble in water. The solution, which is called hydrobromic acid, resembles hydrochloric acid, and is fully dissociated (the discussion of the ionization of hydrochloric acid applies also to this substance). Several hydrates can be isolated by cooling the solutions. The constant-boiling mixture with water boils at $125°$, and contains about 47 per cent hydrogen bromide. Hydrogen bromide is very slowly oxidized by moist oxygen at room temperature.

Bromides.—These may be prepared by methods similar to the first three methods proposed for the chlorides (p. 736), or by the action of bromine on an iodide. They resemble the chlorides in their properties, but are usually, though not always, less volatile; very often the melting- and boiling-points lie between those of the corresponding chloride and iodide.

Oxides.—Bromine was for many years considered to be one of the very few elements which form no oxide. It has, however, recently been proved that unstable oxides are produced by the action of ozone on bromine vapour below 0° C. See also p. 374.

OXYACIDS AND THEIR SALTS.—*Hypobromous acid*, HBrO, and *bromic acid*, HBrO$_3$, are known, and perhaps *bromous acid*, HBrO$_2$, exists, but neither perbromic acid nor a perbromate has been prepared.

Hypobromous acid, HBrO.—Bromine readily dissolves in cold alkaline solutions, forming first a yellow solution of mixed bromide and hypobromite:

$$Br_2 + 2OH' = Br' + BrO' + H_2O.$$

Solutions of the acid can be prepared by shaking bromine water with the oxides of silver or mercury, and purified by distillation; the bromine distils first and may be rejected. Hypobromous acid has never been isolated, and its solutions, which are pale yellow, are unstable; they cannot be concentrated without decomposition. Solutions of hypobromites are powerful oxidizing agents used in organic chemistry to oxidize ammonium compounds, amines, urea,

etc., to nitrogen (and are nearly always prepared for this purpose from bromine and caustic soda):

$$2NH_4^{\cdot}+3BrO'=N_2\uparrow+3H_2O+3Br'+2H^{\cdot}.$$
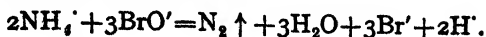
It is surprising to find that alkaline hypobromite solutions are rather stronger oxidizing agents than hypochlorites. This is perhaps because hypobromous acid, a weaker acid than hypochlorous acid, is formed in larger quantities by hydrolysis even of alkaline solutions of its salts.

Bromic acid, $HBrO_3$.—If large quantities of bromine are added to concentrated caustic potash solutions, even in the cold, there is a precipitate of potassium bromate, which is not very soluble in cold water, and can easily be purified by recrystallization:

$$3Br_2+6OH'=BrO_3'+5Br'+3H_2O.$$

It can also be prepared by passing chlorine into an alkaline solution of potassium bromide, bromine being substituted for chlorine in the chlorate which would be produced in the absence of the bromide:

$$Br'+ClO_3'\rightarrow BrO_3'+Cl'.$$
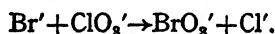
It is best prepared from bromides by electrolysis. Solutions of bromic acid are prepared from solutions of barium bromate and sulphuric acid: the barium bromate is precipitated by mixing boiling saturated solutions of potassium bromate and barium acetate. Like chloric acid, bromic acid has never been isolated in the pure state, and its solutions decompose on heating. They are stronger oxidizing agents than solutions of either chloric or iodic acid, and will convert many organic substances into carbon dioxide and water, and rapidly oxidize sulphur to sulphuric acid.

When the bromates are heated they lose oxygen at fairly low temperatures and are converted to bromides, though the bromates of elements such as aluminium, which have a great affinity for oxygen, may yield a little oxide on ignition. There is no sign of an intermediate formation of perbromate. In solution bromates will oxidize any of the halogen acids, though the hydrochloric acid must be concentrated and none of the reactions is instantaneous, e.g.:

$$2BrO_3'+10I'+12H^{\cdot}=Br_2+5I_2+6H_2O.$$
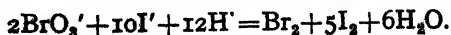
The reaction between bromates and bromides:

$$BrO_3'+5Br'+6H^{\cdot}=3Br_2+3H_2O,$$

which takes place in acid solution, is used in the preparation of standard bromine solutions, and it is important to remember that in dilute solution it proceeds rather slowly.

IODINE

$I=126\cdot91$.   *Atomic Number,* 53

History.—In 1812 a French saltpetre manufacturer, COURTOIS, found that on adding concentrated sulphuric acid to the mother-liquor of the sodium carbonate extracted from the ashes of seaweed, a black powder was precipitated, which on heating was converted into a violet vapour.   Courtois sent some of his new substance to Gay-Lussac, who made a thorough investigation of it and showed that it was an element similar in many respects to chlorine.   He called it *iodine,* from the violet colour of its vapour (Greek ἰοειδής), and succeeded in preparing hydriodic acid, HI, from it.   Sir Humphry Davy, who was passing through Paris at the time, also made investigations on the new element, a specimen of which was given to him by Ampère, and confirmed Gay-Lussac's results.

Occurrence and Extraction.—Iodine is a rare element, but small quantities of iodides occur in sea-water and in various mineral deposits. Small quantities are found in sea plants, and iodine was formerly recovered from them by burning large piles of seaweed and extracting the potassium iodide from the ash.   The process is still worked on a small scale in Japan, but practically all the iodine of commerce is extracted   from   Chile   saltpetre   or   caliche (p. 450), which contains about 0·2 per cent of iodine as sodium iodate, $NaIO_3$.   This remains in   the   mother - liquors left over from the crystallization of the sodium nitrate, and these liquors may contain as much as 20 per cent of the iodate.   They are mixed with a solution of sodium hydrogen sulphite, which precipitates iodine:

FIG. 145. PURIFICA-
TION OF IODINE

$$2IO_3'+2H\dot{}+5HSO_3'=I_2\downarrow+5HSO_4'+H_2O.$$
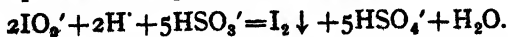
The iodine is washed, pressed, and purified by sublimation.   Commercial iodine may contain water, free or combined chlorine or bromine, and iodine cyanide.   These impurities can be removed by grinding it finely with fresh lime (to remove water) and a little potassium iodide (to retain other halogens), and resubliming it as shown in the diagram.   The mixture is placed in the bottom of a beaker and heated by a small flame, while the upper part of the vessel is filled with a specially shaped condenser full of water

slightly above laboratory temperature. The iodine condenses in beautiful crystals which can readily be detached from the tube by filling it with cold water: they are finely ground and kept in an ungreased desiccator over concentrated sulphuric acid.

The world production of iodine, free and combined, is about two thousand tons per annum, of which some 99 per cent is used in medicine. In recent years it has been discovered that a small quantity of iodine in the body is essential to health, and that some diseases are due to iodine deficiency—goitre, for instance, can be certainly prevented by doses of iodides. The thyroid gland produces an iodine compound (*thyroxin*) which it circulates through the body, and iodine preparations are given with excellent effect to backward children; while fowls dosed with iodine lay more eggs and cattle produce more milk. If given to mares, iodine is said to increase the proportion of twins in their offspring. A tincture of iodine is also used as an antiseptic.

In the laboratory iodine is very widely used in analysis. The reversible change $I_2 + 2$ electrons$\rightleftharpoons 2I'$ is easily carried out without disturbing side-reactions (the standard electrode potential is only $+0.54$ volt), and more than one reaction is available for the estimation of iodine solutions, of which the thiosulphate titration is the most important. Moreover, the smallest quantity of iodine can be detected with the help of the dark blue compound which the free element produces with starch, and this has helped in ' iodimetry ' and ' iodometry,' as iodine titrations are called.

Properties.—Iodine is a bluish-black crystalline solid of density 4.9, melting at $114°$ and boiling at $183°$. The vapour has an intense purple colour by which it can easily be identified. At low temperatures the vapour density corresponds with the formula I_2, but at high temperatures dissociation begins, and reaches 50 per cent at about $850°$. Iodine has a very sharp taste and a faint smell recalling that of chlorine; it is only very slightly soluble in water, to which, however, it gives a very distinct brown colour. A saturated solution at $25°$ contains only some 0.34 gm. per litre. Iodine is, however, much more soluble in solutions of chlorides, bromides, or iodides (the solubility increases in that order), forming complex ions such as I_3' or ClI_2': the investigation of these solutions (first carried out by JAKOWKIN) has already been fully described (p. 200). The chemical properties of the tri-iodide ion are those of a mixture of iodide ions and iodine.

Iodine dissolves in certain organic solvents, such as carbon disulphide, carbon tetrachloride, benzene, or alcohol, much more freely than it does in water, and it can be almost completely extracted from its aqueous solutions by shaking with such of these solvents as are immiscible with water. The solutions are very deeply

coloured; thus a solution in carbon tetrachloride saturated at room temperature, and containing only about 20 gm. iodine per litre, is opaque even in thin layers and appears quite black. This is made use of in iodine titrations. A little carbon tetrachloride is shaken with the titration mixture and loses its pink colour only when the last of the free iodine has been removed. This method is more sensitive than the use of starch.

Non-aqueous solutions of iodine can be divided into two classes according to colour: brown solutions are afforded by the alcohols, ethers, esters, fatty acids, or ketones, violet ones by carbon tetra-chloride, chloroform, carbon disulphide, or hydrocarbons. It will be noticed that the first class of solvents contains those with oxygen in the molecule, and which can act as donors, while the second class contains only indifferent liquids; it is therefore supposed that in the brown solutions iodine is combined with the solvent, but in the violet solutions exists as free molecules. There is some experimental evidence for this view, on which the cryoscopic method, which depends only on the concentration of solute particles, can cast no light:

(i) The violet colour of the solutions is the same as that of iodine vapour, and is almost independent of the nature of the solvent: this is not true of the brown colour.

(ii) There is some tendency on the part of the brown solutions to become violet on heating.

There is other evidence which points in the same direction.

The tincture of iodine used for medicinal purposes is a solution of iodine and potassium iodide in dilute alcohol.

Iodine is the least active of the halogens, and is somewhat inert towards the non-metals, but it combines directly with most of the metals, often with incandescence. A warm mixture of aluminium powder and iodine is fairly stable, but if a drop of water is added to the mixture vigorous combination takes place, with red flames and copious evolution of fumes from the unchanged iodine. Apart from such examples of direct combination, the inorganic reactions of iodine in solution can mostly be classified as: 1. Reductions to iodide. 2. Oxidations to hypoiodite, usually followed by further changes. 3. Simultaneous oxidation and reduction.

1. *Reduction to iodide.*—This can take place, according to the conditions, either by the acquisition of electrons or by the liberation of oxygen atoms from water:

$$I_2 + 2 \text{ electrons} \rightarrow 2I' \quad \text{or} \quad I_2 + H_2O \rightarrow 2I' + 2H^{\cdot} + O.$$
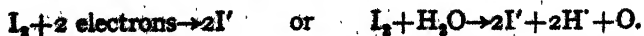
The first change is scarcely affected by alterations in the acidity

of the solution, whereas the second goes best in weakly alkaline solution, and may be reversed if the solution is strongly acid. Examples are the reactions of iodine solutions with thiosulphate and with arsenites:

$$I_2+2S_2O_3''=2I'+S_4O_6''. \quad I_2+H_2O+AsO_3'''=2I'+2H^.+AsO_4'''.$$
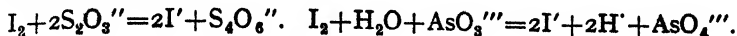
The action with thiosulphates takes place under any conditions of acidity, whereas the arsenite reaction needs careful control, and will not reach completion unless measures are taken to prevent an increase in the hydrogen ion concentration. On the other hand strongly alkaline solutions lead to the formation of hypoiodite, and must equally be avoided. The reaction can be carried out with success if sodium hydrogen carbonate is added to the solution as a buffer. Both reactions are extensively used in volumetric analysis.

2. *Oxidation to hypoiodite.*—Hypoiodous acid is the first product of the oxidation of iodine:

$$I_2+H_2O+O\rightarrow 2HIO,$$
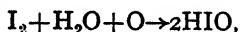
but it is an unstable substance (see below), and is seldom found in the final product. Thus when iodine is boiled with nitric acid of suitable concentration it is quantitatively converted to iodic acid:

$$2I_2+2H_2O+10O=4HIO_3.$$
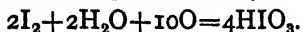
3. *Simultaneous Oxidation and Reduction.*—This takes place when iodine dissolves in solutions of caustic alkali, the first products being an iodide and hypoiodous acid:

$$I_2+OH'\rightarrow HIO+I'.$$
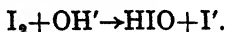
Even in alkaline solution the very weak electrolyte hypoiodous acid soon decomposes into iodate and iodide:

$$3HIO\rightarrow 3H^.+IO_3'+2I',$$
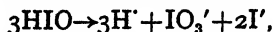
but this can be avoided, to some extent at least, by using a solution with a very low hydroxyl ion concentration, e.g. a suspension of mercuric oxide. This indeed is the best method of preparing a solution of hypoiodous acid; the mercuric iodide is removed by filtration:

$$2I_2+HgO+H_2O=HgI_2\downarrow +2HIO.$$
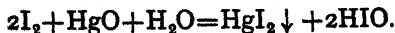
In spite of its instability hypoiodous acid is the key to much of the solution chemistry of iodine, and its methods of decomposition must be further examined.

It differs from the analogous compounds of chlorine and bromine in being amphoteric: it is simultaneously hypoiodous acid and iodine hydroxide. Consequently it can decompose in more than one way:

(i) In alkaline solutions it yields an iodate and an iodide:

$$3HIO \rightarrow 3H^{\cdot} + IO_3' + 2I'.$$
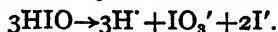
This reaction may also take place in weakly acid solution, and then goes farther, for in acid solution iodates will oxidize iodides:

$$IO_3' + 5I' + 6H^{\cdot} = 3I_2 + 3H_2O,$$
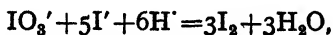
so that the entire change is then:

$$5HIO = HIO_3 + 2I_2 + 2H_2O.$$
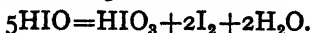
(ii) If the unstable neutral solution is brought into contact with easily oxidizable substances (such as the salts of manganese or cobalt), decomposition takes place as follows:

$$HIO \rightarrow H^{\cdot} + I' + O,$$
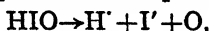
and oxidized substances (such as sesquioxides of manganese or cobalt) are produced.

(iii) In *very strongly acid* solution hypoiodous acid ionizes as a base:

$$IOH + H_2O = (I.H_2O)^{\cdot} + OH',$$
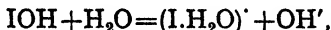
and produces solutions containing positive iodine. See p. 724.

Hydrogen iodide, HI. — The reaction between hydrogen and iodine, one of the simplest and most easily accessible examples of chemical equilibrium, has been exhaustively investigated by BODENSTEIN, and by others after him (p. 111). The synthesis of hydrogen iodide can be carried out in the laboratory, but even with the help of platinized asbestos the process is inconvenient. A better method is to treat iodine and water with small quantities of red phosphorus, made into a paste with water and dropped on to them through a tap-funnel. By using excess of iodine it is possible to avoid the formation of phosphonium iodide and to carry out the reaction according to the equation:

$$P + 5I + 4H_2O = 5HI \uparrow + H_3PO_4.$$
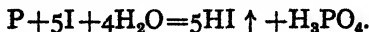
The gas is washed with a very small quantity of water, and is freed from iodine vapour by passing it over moist phosphorus. It may be dried with calcium iodide or phosphorus pentoxide, but not with calcium chloride, which produces a little hydrogen chloride.

A solution of hydrogen iodide can conveniently be made by adding small quantities of iodine to water through which bubbles a stream of hydrogen sulphide:

$$H_2S + I_2 = 2HI + S \downarrow .$$
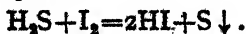
The sulphur is filtered off and the hydrogen sulphide, which is much less soluble in water than is hydrogen iodide, is removed by

a current of carbon dioxide followed by boiling. The solution can be concentrated by boiling off the water until the constant-boiling mixture remains in the distillation vessel; it contains 57 per cent hydrogen iodide and boils at about 127°.

Since iodides are oxidized by hot concentrated sulphuric acid, this acid cannot be used for the preparation of hydrogen iodide.

Properties.—Hydrogen iodide is a colourless gas with a pungent smell, freezing at —51° and boiling at —35°; it is exceedingly soluble in water. The solution is called hydriodic acid, and is a strong acid: the remarks on the ionization of hydrochloric acid apply to this substance also. Hydrogen iodide differs from the other hydrogen halides in dissociating into its elements at much lower temperatures. At 300° the dissociation has already reached 18 per cent, so that the colour of iodine vapour is apparent even at lower temperatures than this. The dissociation of the other hydrogen halides at 300° is very slight indeed. The aqueous solution is easily oxidized to iodine and water, and this is brought about by the action of the air, so that hydriodic acid, unless isolated from the atmosphere, fairly rapidly becomes yellow. Solutions of other iodides become yellow for a similar reason, for the carbon dioxide of the air, by dissolving in water, provides a sufficient concentration of hydrogen ions to make the change possible.

Iodides.—These are usually prepared:

(i) by direct combination:

(ii) less often by the action of hydrogen iodide, free or in solution, on the metal, oxide, or carbonate;

(iii) by acting on a hot oxide of a metal with iodine vapour, e.g.:

$$2PbO + 2I_2 \rightleftharpoons 2PbI_2 + O_2;$$

(iv) by reducing an iodate or periodate, often simply by heating it.

Iodides are usually less volatile than the bromides or chlorides of the same element, and they are more often coloured; the occurrence of insoluble iodides is also more frequent. Iodine is so easily liberated from solutions of iodides that the iodides of oxidizing cations (in which we may include the noble metals) either cannot be prepared or are insoluble in water; thus ferric, cupric, and ceric iodides are unknown, and cuprous, silver, auric, mercurous, and mercuric iodides are insoluble.

The oxidation of iodide solutions to iodine can be carried out with a large variety of reagents, and the estimation of iodine by the thiosulphate titration is at once so accurate and so convenient that this reaction is often used for the estimation of oxidizing substances. Chlorine, bromine, dichromates, permanganates, hydrogen peroxide, and metallic peroxides can all be estimated in this way, as well

as iodates (see below). Some of these reactions do not take place instantaneously; they may then be accelerated with a catalyst such as a molybdate or a tungstate, ammonium molybdate being commonly used for the purpose in the case of hydrogen peroxide. Solid iodides are more easily decomposed by heating in air or oxygen than are the other halides. In such decompositions iodine escapes and an oxide is left.

OXIDES OF IODINE.—The principal oxides of iodine are the dioxide, IO_2, and the pentoxide, I_2O_5; but another of formula I_4O_9 certainly exists (see p. 724), and others have been reported.

Iodine dioxide, IO_2 or I_2O_4, is prepared from iodic acid by heating it with excess of concentrated sulphuric acid: oxygen is given off and a brown solid remains which can be washed with water and dried at 100°. The pure dioxide is a yellow solid which decomposes when heated much above this temperature, and which in contact with moist air, or when treated with water, forms iodine and iodic acid:

$$10IO_2 + 4H_2O = I_2 + 8HIO_3.$$
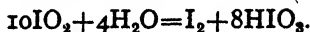
Iodine pentoxide, Iodic anhydride, I_2O_5, is prepared by heating iodic acid to 240°. It is a white deliquescent solid readily soluble in water, with which it forms iodic acid, and rapidly dissociating into iodine and oxygen if heated to 300° or over. It is insoluble in organic solvents.

Iodine pentoxide has the oxidizing properties of iodic acid, and reacts with easily oxidizable substances with inflammation. It is used in the estimation of carbon monoxide in air or other gas mixture. The carbon monoxide is oxidized to carbon dioxide, which can easily be absorbed in baryta and estimated:

$$I_2O_5 + 5CO = I_2 + 5CO_2.$$
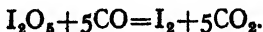
Other Oxides.—Iodine, whether in the solid state, as vapour, or dissolved in organic liquids, is attacked by ozone with the formation of solid oxides to which various formulae have been assigned. The product is very possibly *iodine iodate*, I_4O_9 or $I(IO_3)_3$, mixed with other oxides, but this conclusion is not certain. Whatever its nature, it loses iodine on heating, and on treatment with water yields iodine and iodic acid.

OXYACIDS OF IODINE.—These are hypoiodous acid, HIO, iodic HIO_3, and periodic acid, HIO_4.

acid, HIO.—The preparation of this substance by oxidation of iodine in the presence of water has already been discussed, as also its decomposition. The hypoiodites are less stable even than the corresponding compounds of bromine.

Iodic acid, HIO_3, and the Iodates.—Iodic acid can be prepared without difficulty by heating iodine with concentrated nitric acid.

The residue is dissolved in water and heated to dryness once or twice to remove all the nitric acid. A simple but less convenient method of obtaining the compound is by the hydrolysis of iodine chloride, or by the equivalent operation of passing chlorine through a suspension of iodine in water:

$$I_2+5Cl_2+6H_2O=2HIO_3+10HCl.$$
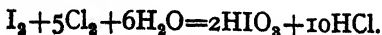
The hydrochloric acid is removed with silver oxide. Iodine will displace chlorine from chloric acid:

$$I_2+2ClO_3'=2IO_3'+Cl_2\uparrow,$$
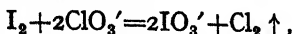
and solutions of iodic acid can be prepared by this method.

Iodic acid is a colourless crystalline solid, hygroscopic, and exceedingly soluble in water. The solutions are strong acids. The solid loses water at 110° to form a compound, $I_2O_5.HIO_3$, and at 240° is completely converted to the pentoxide.

Potassium iodate, KIO_3, can be prepared by warming a solution of potassium chlorate, initially containing a small amount of chlorine, with iodine, when the successive reactions are:

$$(1)\ I_2+Cl_2=2ICl,\qquad (2)\ KClO_3+ICl=KIO_3+Cl_2.$$
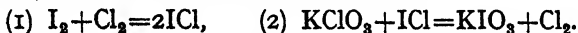
It is a colourless solid, not very soluble in cold water, but very soluble in hot water, and can so readily be obtained in a state of high purity by recrystallization that it is much used as a standard oxidizing substance in volumetric analysis. It melts at 560° and at a slightly higher temperature decomposes into iodide and oxygen: this is the best method of preparing pure potassium iodide.

Sodium iodate, $NaIO_3$, occurs naturally in small quantities in Chile saltpetre (p. 450), which is the source of most of the iodine of commerce.

Barium iodate, $Ba(IO_3)_2.H_2O$, is prepared by precipitation from barium solutions and iodate solutions, as it is nearly insoluble in water. On heating, it first loses its water of crystallization, and then forms barium periodate (or paraperiodate) with the loss of iodine and oxygen:

$$5Ba(IO_3)_2=Ba_5(IO_6)_2+4I_2\uparrow+9O_2\uparrow.$$

Like the chlorates, the iodates are all powerful oxidizing agents. With acid iodide solutions they immediately liberate iodine:

$$IO_3'+5I'+6H^{.}=3I_2+3H_2O,$$
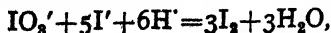
a reaction which can be used for the volumetric analysis of either iodates, iodides, or acids by keeping the other two reactants in excess. This is one of the most accurate methods for the estimation of strong acids in very dilute solution ($N/1000$ or less). In very concentrated hydrochloric acid the addition of more iodate leads

to the formation of iodine monochloride, but if no iodine is present chlorine is given off and iodine trichloride produced:

$$IO_3' + 6HCl = ICl_3 + Cl' + Cl_2 \uparrow + 3H_2O.$$
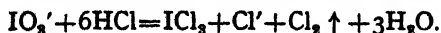
Reducing substances such as phosphorus or sulphur dioxide are immediately oxidized by iodic acid.

The formation of acid salts, of which several are known, is a property of iodic acid which is not shared by chloric or bromic acids, and in concentrated solution the acid itself, or its anion, shows some evidence of association. Thus *potassium di-iodate*, $KIO_3.HIO_3$, and *potassium tri-iodate*, $KIO_3.2HIO_3$, can both be isolated from solutions of potassium iodate and iodic acid.

Periodic acid, HIO_4, and the Periodates.—These compounds are usually obtained by oxidation of iodates. Thus a good yield of the compound $Na_2H_3IO_6$ (*disodium trihydrogen paraperiodate*) can be obtained by passing chlorine into a boiling solution of caustic soda containing excess of iodine. The sodium salt is not very soluble and can be removed by filtration. It can be converted to the still less soluble *silver periodate*, Ag_5IO_6, with the help of silver nitrate solution, and from this compound a solution of periodic acid can be obtained by treatment with chlorine, which precipitates all the silver as chloride.

Alternatively *barium paraperiodate*, $Ba_5(IO_6)_2$, may be obtained as described above by heating the easily-made barium iodate, and a solution of periodic acid can be made from it by treatment with dilute sulphuric acid. From such a solution the pure acid may be obtained by evaporation followed by desiccation over concentrated sulphuric acid: it appears in colourless crystals which have the composition H_5IO_6 (or $HIO_4.2H_2O$) and are known as *paraperiodic acid*. If subjected to prolonged heating at 100° in a vacuum they lose water and are completely converted to the *meta*-acid, HIO_4.

The basicity of periodic acid in its various forms is not yet completely understood. If titrated against strong bases it is monobasic with methyl orange and dibasic with thymolphthalein. The conductivity results also point to the conclusion that paraperiodic acid is fairly strong in its first dissociation, weak in its second dissociation, and very weak in the others. The solid periodates are a complicated series of salts which can be regarded as derivatives, often hydrated, of the two known forms of the acid, HIO_4 and H_5IO_6, but others prefer to derive some at least from a hypothetical acid, $H_4I_2O_9$ (or $2HIO_4.H_2O$). Thus disodium trihydrogen paraperiodate may be $Na_2H_3IO_6$ or $Na_4I_2O_9.3H_2O$. Whatever view be taken of these matters, there is no difficulty in formulating periodic acid and its salts as compounds of a hypothetical acid anhydride, iodine heptoxide, I_2O_7, with varying proportions of water or a base.

The periodates are stable compounds, though powerful oxidizing agents. Barium paraperiodate, obtained by heating barium iodate, can be kept for considerable periods at a red heat without much decomposition. Periodates liberate the whole of their iodine when treated with acid iodide solutions, and this can be used in their estimation:

$$IO_4' + 7I' + 8H^{\cdot} = 4I_2 + 4H_2O.$$
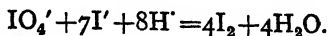
Potassium metaperiodate, KIO_4, is obtained from chlorine and hot alkaline potassium iodate; like potassium perchlorate, it is only slightly soluble in cold water. On heating, it forms first potassium iodate (contrast potassium perchlorate), then potassium iodide.

Disodium trihydrogen paraperiodate, $Na_2H_3IO_6$, is prepared as described above. From solutions of this salt in aqueous periodic acid the compounds $NaIO_4$ and NaH_4IO_6 can be obtained by crystallization, while from strongly alkaline solutions $Na_3H_2IO_6$ is deposited. *Normal sodium paraperiodate*, Na_5IO_6, has also been described, and the existence of similar salts of silver and barium is beyond question.

Iodine monochloride, ICl, is obtained without difficulty by union of the elements. Chlorine is passed over iodine until the product is liquid, and the monochloride is purified by distillation. It is a frequent product of reactions in which chlorine is liberated in the presence of iodine, or vice versa, provided that water is absent, and can, for example, be prepared by distilling a mixture of iodine and potassium chlorate:

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2, \text{ followed by } Cl_2 + I_2 = 2ICl.$$
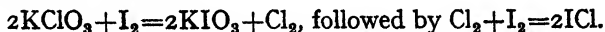
It is hydrolysed by water with the production of iodine and iodic acid:

$$5ICl + 3H_2O \rightleftharpoons 2I_2 + HIO_3 + 5HCl,$$
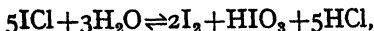
but the reaction is reversible, and in the presence of very concentrated hydrochloric acid an iodate will oxidize iodine quantitatively to form a pale yellow and very stable solution containing the anion ICl_2':

$$ICl + Cl' = ICl_2'.$$
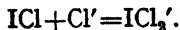
Potassium iodate, acting in the presence of much hydrochloric acid, has become widely used as a quantitative oxidant in volumetric analysis (for example, in ANDREWS' method). Its action is based on the equation:

$$IO_3' + 6H^{\cdot} + 2Cl' + 4e = ICl_2' + 3H_2O,$$
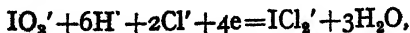
from which it is seen that under the conditions specified the oxidation equivalent of iodate is one fourth of the formula weight.

Iodine monochloride is a red solid which exists in two forms, melting at $27°$ and $14°$ to a brown liquid. This liquid boils at about $100°$ to form a red vapour which is not markedly dissociated.

Iodine monochloride dissolves in organic solvents to form deeply coloured solutions, from which, however, it can be extracted by water, which decomposes it, or by hydrochloric acid, which changes it to ICl_2'. Its chemical activity exceeds that either of iodine or of chlorine, and it finds some use in the laboratory as a chlorinating agent, e.g. in destroying any carbon disulphide which may be present in commercial carbon tetrachloride, and as a catalyst or ' chlorine carrier.' It combines with alkali-metal halides, particularly those of rubidium or caesium, to form compounds such as $CsICl_2$, containing polyhalide ions.

Iodine monobromide, IBr, is obtained by combination of the elements. It is a solid not unlike iodine in appearance but smelling of bromine; it melts at 42° and boils at 116°. It resembles iodine monochloride in its chemical properties, but is less stable.

Iodine cyanide, ICN, is produced by the action of potassium iodate on iodine in the presence of cyanides, or by adding iodine in theoretical amount to a well-cooled aqueous solution of sodium cyanide, followed by extraction of the iodine cyanide with ether, and its recrystallization from chloroform. It is very poisonous, and dissolves only slowly in water. The action:

$$ICN + I' \rightleftharpoons I_2 + CN',$$
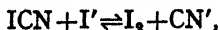
is reversible. Acids reduce the concentration of cyanide ion by forming the very weak hydrocyanic acid, and so in acid solution iodine cyanide will oxidize iodides to iodine. In neutral solution the reverse change takes place.

Although it is very improbable that iodine cyanide and the halides described above actually contain the cation I˙, some of their reactions can be most easily explained by assuming a mechanism involving fission into the appropriate anion and such a cation, perhaps temporarily stabilized as suggested on p. 724.

Iodine trichloride, ICl_3.—The best-known of the compounds of tervalent iodine is iodine trichloride, ICl_3, produced from iodine and excess of chlorine. If the reaction mixture is warmed, the trichloride collects in yellow crystals in the cooler parts of the apparatus. It is a solid which melts at 25°, and readily decomposes on warming into the monochloride and chlorine. It is hydrolysed by water, but the reaction is not reversible. If the water is in large excess the principal reaction is:

$$5ICl_3 + 9H_2O = 15HCl + 3HIO_3 + I_2,$$
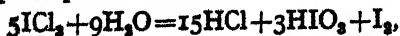
but other products may be formed. The hydrolysis can be prevented by a sufficient concentration of hydrochloric acid. Iodine trichloride forms a series of salts, such as $CsICl_4$, with the halides of the alkali-metals; these salts are stable, brilliantly coloured substances which can be recrystallized from water. *Rubidium tetra-*

chloro-iodite, RbICl$_4$, is obtained in bright yellow crystals by passing excess of chlorine into a concentrated solution of rubidium iodide:

$$RbI + 2Cl_2 = RbICl_4 \downarrow ,$$
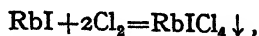
and cooling the solution. The corresponding acid, HICl$_4$.4H$_2$O, is precipitated as orange-yellow crystals when chlorine is passed through a suspension of iodine in concentrated hydrochloric acid at 0°. It was doubted whether such compounds as RbICl$_4$ contain the iodine in the anion, as they lose iodine on extraction with organic solvents; but KICl$_4$ has been X-rayed and shows a square-shaped anion:

$$
\begin{array}{cc}
Cl & Cl \\
\\
\\
Cl & Cl
\end{array}
$$

Iodine acetate, I(CH$_3$.COO)$_3$, can be prepared by oxidizing iodine dissolved in glacial acetic acid with chlorine monoxide:

$$I_2 + 6CH_3.COOH + 3Cl_2O = 2I(CH_3.COO)_3 + 3H_2O + 3Cl_2.$$
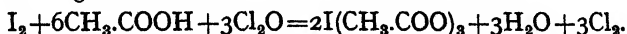
Iodine nitrate, probably I(NO$_3$)$_3$, can be prepared from iodine and very concentrated nitric acid; it is a yellow powder decomposed by water.

Iodine sulphates of uncertain constitution have been prepared by the action of concentrated sulphuric acid on iodic acid.

SUBGROUP A

MANGANESE, TECHNETIUM, RHENIUM

Mn=54·94; *atomic number*, 25   Tc=(99); *atomic number* 43
Re=186·22; *atomic number*, 75

Manganese is the only important element of this subgroup. The discovery of 'masurium' was announced in 1925, but has not been confirmed. An element, named *technetium*, undoubtedly an isotope of atomic number 43, with mass number 99, has been identified in the products of bombarding molybdenum with deuterons. It closely resembles rhenium. Rhenium also was not discovered till 1925, but our knowledge of this rare element is now fairly complete.

The atomic numbers, atomic weights, densities, and atomic volumes are as follows:

	Mn	*Tc*	*Re*
Atomic Number	25	43	75
Atomic Weight	54·94	?	186·22
Density	7·06	?	21·4
Atomic Volume	7·8	?	8·8

2 B

MANGANESE

$Mn = 54.94$.   *Atomic Number*, 25

History.—Although pyrolusite (MnO_2) has been used for perhaps two thousand years in glass manufacture (to obscure the green colour caused by the presence of iron), metallic manganese was first prepared in 1774, when GAHN obtained it by reducing pyrolusite with carbon.   In early times, pyrolusite was confused with magnetite and other black minerals, and it is rare to find any even moderately accurate account of its properties before the eighteenth century.

Occurrence and Extraction.—Manganese is neither very abundant nor very scarce, one or two million tons of the ores being produced annually.   They are widely diffused, and usually consist of the oxides, contaminated with iron and other metals, though the sulphide, *manganese blende*, MnS, is well known.   The principal ore is *pyrolusite*, MnO_2, found in Germany and other parts of Europe, in America, and in Africa.   Another common ore is *braunite*, Mn_2O_3.   Traces of manganese compounds are found in many plants and animals.

Most of the manganese of commerce is in the form of an alloy with iron called *ferro-manganese*, which can be made in a blast furnace by the reduction of mixed oxides of manganese and iron, with a large quantity of lime as flux.   In the laboratory the metal can be obtained by the reduction of its compounds with powerful reducing agents.   Carbon has often been used, but it requires a very high temperature, and the metal produced contains carbide. The reduction of manganese oxides with hydrogen likewise requires a very high temperature, and on a small scale the action of magnesium on a fused mixture of manganese and potassium chlorides is to be preferred.   The metal can also be obtained electrolytically. But by far the most convenient method for the preparation of pure manganese on a large scale or in the laboratory is the GOLDSCHMIDT process (p. 533), in the course of which the metal fuses and collects in a compact form at the bottom of the containing vessel.

Ferro-manganese is used as a deoxidizer in the Bessemer process for making steel (p. 772).   Steel containing a small proportion of manganese is exceptionally hard, and is used in steam navvies crushing machinery, safes, and for similar purposes.

Properties.—Pure manganese is a silver-white metal with a density of 7·06, melting at 1245°.   It is hard, but not so hard as cast iron.   Pure manganese is stable in the air, but if it contains carbide or other impurities it is easily corroded.   The standard electrode potential, though not very accurately known, is in the

neighbourhood of -1.08 volts, so in the electrochemical series manganese comes between zinc and aluminium. It reacts very slowly or not at all with cold water, forming manganous hydroxide, $Mn(OH)_2$, and is easily dissolved by dilute acids, with which it forms manganous salts. It does not display passivity in concentrated nitric acid. The metal combines with the halogens, sulphur, and phosphorus, and with nitrogen on strong heating. Like many other metals, it can be prepared in a pyrophoric form by heating the amalgam under reduced pressure or by other processes.

OXIDES AND HYDROXIDES.—The oxides of manganese are given in the table. Manganese can have all valencies from two to seven except five, and the complexity of its valency relations makes the study of this element a difficult one.

Manganous oxide, MnO, a strongly basic oxide corresponding with the manganous salts.

Manganic oxide, Mn_2O_3, weakly basic and corresponding with the manganic salts.

Trimanganese tetroxide, Mn_3O_4, with no corresponding series of salts.

Manganese dioxide, MnO_2, weakly acidic and corresponding with the manganites.

Manganese heptoxide, Mn_2O_7, strongly acidic and corresponding with the permanganates.

No manganese trioxide corresponding with the manganates exists (see p. 763).

THE OXIDES OF MANGANESE

Manganous hydroxide, $Mn(OH)_2$, is a colourless solid precipitated from manganous solutions by caustic alkalis. As it is not among the least soluble of metallic hydroxides, a large concentration of ammonium ions will prevent its precipitation by ammonia. When exposed to the air it becomes brown and is oxidized to hydrated manganese dioxide.

Manganous oxide, MnO, is a grey or greenish substance prepared by heating the hydroxide in the absence of air (e.g. in hydrogen) or by reducing with hydrogen any other oxide of manganese. It can be reduced to the metal only with the greatest difficulty, which accounts for its use as a deoxidizer in the manufacture of iron. With hydrogen a temperature of over 1200° is required. If finely divided and warm the oxide may be pyrophoric, and if heated in steam it will reduce it with the formation of hydrogen and trimanganese tetroxide.

Manganic oxide, Mn_2O_3, occurs in nature in the hydrated form as *manganite*, and anhydrous as *braunite*. The hydrated form can conveniently be obtained by passing a brisk current of air for some hours through an ammoniacal solution containing a manganous salt and ammonium chloride.   Manganic oxide is a black solid which can be heated in the air without change to nearly 1000°, but above that temperature gives up oxygen to form trimanganese tetroxide (compare iron).   It is easily reduced to the monoxide by heating in hydrogen.   With concentrated acids it yields solutions of manganic salts.   The stability of these solutions depends on the nature of the anion, but they usually decompose on heating, liberating oxygen or an oxidation-product of the anion—e.g. chlorine from hydrochloric acid.   Boiling with dilute acids, if these are not easily oxidized, produces a manganous solution and a precipitate of hydrated manganese dioxide:

$$Mn_2O_3 + 2H^{\cdot} = Mn^{\cdot\cdot} + MnO_2\downarrow + H_2O.$$
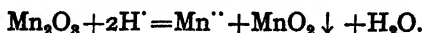
Trimanganese tetroxide, Mn_3O_4, is the stable oxide of manganese at high temperatures, and can be prepared by heating any other oxide to 1000° or over.   The colour depends on the method of preparation and the state of subdivision.   In the hydrated form it can also be precipitated by caustic alkalis from mixed manganous and manganic solutions.   With acids, like the sesquioxide, it yields a mixture of a manganous salt and manganese dioxide, which may or may not oxidize the acid.   Trimanganese tetroxide is composed of the simple ions $Mn^{\cdot\cdot}$, $Mn^{\cdot\cdot\cdot}$, and O'', and is the analogue of Fe_3O_4 and Co_3O_4.

Manganese dioxide, MnO_2, occurs in nature as pyrolusite, the principal ore of manganese.   In the hydrated form it can be produced from solutions of manganese compounds by many different reactions.   Manganous salts can be oxidized in alkaline, neutral, or even dilute acid solution, with a hypochlorite, sodium peroxide, or at the anode in electrolysis.   Permanganates can be reduced in alkaline solution with hydrogen peroxide, or by manganous salts, or by boiling with ammonia.   The anhydrous oxide can be made by heating the hydrates at a carefully regulated temperature, or by heating manganous nitrate in the air and extracting any lower oxides with concentrated nitric acid.

 Manganese dioxide is a brown or black substance nearly insoluble in water, but a suspension of the hydrated form will redden blue litmus.   When strongly heated it yields at about 600° the sesquioxide and oxygen; further heating in air converts the sesquioxide to trimanganese tetroxide.   Manganese dioxide can be reduced without difficulty to the monoxide by heating in hydrogen or in nitric oxide, while gaseous ammonia will reduce it to the sesquioxide.

The dioxide is insoluble in some acids, such as hydrofluoric acid, while with other acids it forms a solution which contains either ter- or quadrivalent manganese. Such a solution decomposes on heating to form a manganous solution and either oxygen or an oxidation-product of the acid anion, so that in boiling concentrated solution sulphuric acid gives oxygen and hydrochloric acid chlorine. This is one of the commonest methods of preparing chlorine. The dioxide will not dissolve in aqueous alkalis, though it takes up alkali from the solution to form an insoluble manganite. Fusion with caustic alkali likewise converts some of it to a manganite. Powerful oxidizing agents, such as hypochlorites, act on alkaline suspensions of manganese dioxide to form a permanganate:

$$2MnO_2 + 2OH' + 3O = 2MnO_4' + H_2O.$$
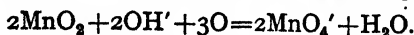
The dioxide is a catalyst for many reactions in which oxygen is evolved. It is widely used in the laboratory to assist the decomposition of potassium chlorate, and it rapidly converts hydrogen peroxide solutions into oxygen and water. It is noteworthy that the dioxides MO_2 of titanium, germanium, tin, lead, and manganese all possess a common type of ionic crystal structure, wherein six oxygen ions, O'', surround a metal ion, M'''', and three metal ions an oxygen ion.

Manganese dioxide is used in the manufacture of potassium permanganate, and was formerly employed in the WELDON chlorine process and in the manufacture of bromine.

Manganese trioxide.—In view of the close relationship of manganates to sulphates and chromates it was to be expected that manganese would yield a trioxide. Such an oxide was formerly thought to be produced, as a reddish vapour, when a solution of potassium permanganate in cold concentrated sulphuric acid was dropped slowly upon sodium hydrogen carbonate. A recent re-examination has shown that nothing can be isolated from the red vapour but permanganic acid, of which, in droplets, the 'vapour' consists. Further, in the careful thermal decomposition of the heptoxide, Mn_2O_7, no intermediate oxide can be detected before the final residue of dioxide. If the trioxide can exist it has certainly not yet been obtained.

Manganese heptoxide, Permanganic anhydride, Mn_2O_7.—This very unstable substance separates in dense drops of a dark colour when finely-powdered potassium permanganate is added to well-cooled anhydrous sulphuric acid:

$$2HMnO_4 - H_2O = Mn_2O_7.$$
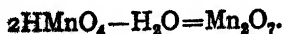
It is rapidly decomposed by moisture, but dilute solutions can be prepared. They have the familiar purple colour and contain

permanganic acid, $HMnO_4$. The action of dilute sulphuric acid on a solution of barium permanganate is a more convenient method of preparing the acid solution. Manganese heptoxide is a very powerful oxidizing agent.

MANGANOUS COMPOUNDS.—In the manganous compounds the element is bivalent; this is the stablest cation of manganese. Manganous compounds resemble the ferrous compounds and are produced by the action of acids on the metal, by the action of all the halogens, except fluorine, on the metal, by the reduction, often very easily effected, of more highly oxidized manganese compounds, and in various other ways. The manganous ion is pale pink. Since the hydroxide is a strong base, there is no perceptible hydrolysis of the salts at room temperature.

The oxidation of manganous compounds can lead to the formation of manganic compounds, manganese dioxide, or permanganates. Manganic salts can exist only in solutions very concentrated in some acid resistant to oxidation, or containing the metal in a complex anion. If these conditions are not satisfied, manganese dioxide is precipitated, unless the oxidizing agent is able to oxidize it still further to a permanganate. The oxidation to manganese dioxide (or sesquioxide) is much more easily effected in alkaline than in acid solution, as would be expected from the equation:

$$Mn^{\cdot\cdot}+O+2OH'=MnO_2\downarrow+H_2O,$$
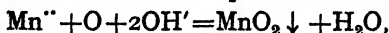
and manganous hydroxide is oxidized to manganese dioxide merely by exposure to the air. If a permanganate is to be produced, it is essential that the manganous solution should be dilute, for otherwise the permanganate reacts with unchanged manganous ions to form the dioxide:

$$2MnO_4'+3Mn^{\cdot\cdot}+4OH'=5MnO_2\downarrow+2H_2O.$$

These influences may be illustrated by the behaviour of ozone, which in concentrated sulphuric acid produces manganic sulphate, in concentrated hydrochloric acid chlorine, in dilute acid very dilute in manganous salt a permanganate, and in neutral solutions of moderate concentration manganese dioxide. Chlorine or bromine produce manganese dioxide or a permanganate, hydrogen peroxide or sodium peroxide produce manganese dioxide, while a mixture of lead dioxide and nitric acid produces a permanganate, provided the manganous solution is dilute.

MANGANOUS HALIDES.—These salts are prepared by the usual methods. If they are required anhydrous, evaporation of the aqueous solution is best conducted in a current of the hydrogen halide. Like other manganese compounds, they can be reduced to the metal with hydrogen only at very high temperatures.

Manganous fluoride, MnF_2, is a rose-coloured salt with a high

melting-point, nearly insoluble in water. Boiling with water produces an oxyfluoride.

Manganous chloride, $MnCl_2$, is a very deliquescent rose-coloured salt which melts at 650° and can be boiled at a very high temperature. The vapour density corresponds with the simple formula. It is very soluble in water and forms numerous hydrates; it also dissolves in alcohol, but not in ether. It was used in the Weldon chlorine process (p. 731), and is a good catalyst for the chlorination of carbon disulphide.

Manganous bromide, $MnBr_2$, and **iodide,** MnI_2, resemble the chloride, but are more readily converted to trimanganese tetroxide on heating in the air.

Manganous carbonate, $MnCO_3$, is prepared by adding a bicarbonate solution to a manganous solution which is kept saturated with carbon dioxide. This precaution is necessary because manganous hydroxide is a good deal less soluble than the carbonate, and a normal carbonate solution precipitates a mixture of hydroxide and carbonate. The presence of hydroxide in the white precipitate obtained is easily revealed by the brown colour produced by exposure to the air. The carbonate is decomposed by boiling water into the hydroxide and carbon dioxide, and is easily decomposed by heating alone.

Manganous nitrate, $Mn(NO_3)_2$, is obtained in solution by the usual methods, but if the neutral solutions are evaporated the oxidizing action of the hot concentrated nitrate solution produces manganese dioxide. Various hydrates of the nitrate, or the anhydrous salt, can be prepared by cautious concentration of nitric acid solutions. At room temperature the colourless hexahydrate, $Mn(NO_3)_2.6H_2O$, is the stable modification. It is very soluble in water. The anhydrous salt begins to decompose at 160°.

Manganous phosphate, $Mn_3(PO_4)_2.7H_2O$, is precipitated as a colourless solid nearly insoluble in water by the addition of soluble phosphates, such as disodium hydrogen phosphate, to manganous solutions.

Manganous sulphide, MnS, is prepared by precipitation in neutral or alkaline solutions, or by heating manganous oxide in hydrogen sulphide. It occurs in a pink crystalline form, and when amorphous may be orange or green. It is more soluble than ferrous sulphide, and cannot be precipitated from acid solution. Heated in the air, it yields sulphur dioxide and trimanganese tetroxide.

Manganous sulphate, $MnSO_4$, is one of the commonest compounds of manganese, and is prepared from natural manganic oxide and sulphuric acid or by the other usual methods. The pentahydrate, $MnSO_4.5H_2O$, isomorphous with copper sulphate pentahydrate, is deposited on cooling the solutions to room temperature, and loses

all its water at 280°. Manganous sulphate is very nearly colourless, and dissolves readily in water, but not in alcohol. It melts at 700°, and at higher temperatures, in the air, yields trimanganese tetroxide.

Manganocyanides.—These compounds contain the ion $Mn(CN)_6''''$ and resemble the ferrocyanides in composition, but they are much less stable. *Potassium manganocyanide*, $K_4Mn(CN)_6.3H_2O$, is prepared by dissolving manganous hydroxide in potassium cyanide solution and allowing the liquid to crystallize in the cold. The action is reversed on boiling with water. Exposure to the air converts manganocyanides in solution to manganicyanides.

MANGANIC COMPOUNDS.—The oxidation potential of the change $Mn^{···} \rightarrow Mn^{··}$, though not accurately known, greatly exceeds the ferric-ferrous oxidation potential of 0·77 volt, and is probably more than 1·5 volts (both with respect to the hydrogen electrode). It follows that manganic salts are powerful oxidizing agents, but concentrated solutions of manganic salts cannot be prepared on account of the tendency of the manganic ion to react with water, forming a manganous ion and manganese dioxide:

$$2Mn^{···} + 2H_2O = Mn^{··} + MnO_2 \downarrow + 4H^{·},$$
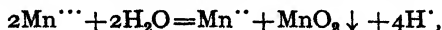
a tendency which can be prevented only by concentrated acids. Solutions of manganic salts have an acid reaction from hydrolysis, and may deposit the sesquioxide unless acid is added to them. Manganic solutions are therefore stable, even in the cold, only in the presence of a large excess of an acid difficult to oxidize, unless the tervalent manganese is present in a complex anion. Insoluble manganic compounds, such as the oxide Mn_2O_3, or the phosphate $MnPO_4$, are, on the contrary, usually stable. The extreme insolubility of the dioxide or its hydrate causes manganous hydroxide to be a powerful reducing agent (compare the similar powers of ferrous hydroxide). Indeed the relationship between manganous and manganic compounds recalls in many ways that between ferrous and ferric compounds. The stability of the manganifluoride complex, $(MnF_5.H_2O)''$, is a further point of similarity, and in the presence of excess of fluoride ions manganous salts will reduce iodine to iodide.

HALIDES.—The manganic-manganous oxidation potential exceeds the standard electrode potentials of all the halogens except fluorine.

Manganic fluoride, MnF_3, is prepared by the action of fluorine on manganese or the manganous halides. On heating it gives manganous fluoride and fluorine. It dissolves in water to form an unstable red solution which deposits manganese dioxide, but in the presence of excess of fluoride ions a stable manganifluoride solution is produced. This is much more easily prepared by the

action of a permanganate on a manganous solution containing excess of fluoride:

$$MnO_4' + 4Mn^{..} + 25F' + 8H^. = 5MnF_5.H_2O'' + 3H_2O.$$
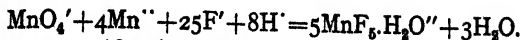
Potassium manganifluoride, $K_2MnF_5.H_2O$, is slightly soluble in water and can easily be precipitated from the solution. It is slowly decomposed by water to form manganic oxide.

Manganic chloride, $MnCl_3$, is unknown in the solid state, but can be extracted by ether, in which it forms a violet solution, from a solution of manganese dioxide in cold concentrated hydrochloric acid. *Potassium manganichloride*, $K_2MnCl_5.H_2O$, is a red solid resembling the manganifluoride in its properties.

Manganic sulphate, $Mn_2(SO_4)_3$, is obtained by treating manganese dioxide with concentrated sulphuric acid and a little manganous salt as catalyst, warming till no more oxygen is evolved, washing with concentrated nitric acid, and drying at 150°. It is a green, very deliquescent solid, stable in dry air. It dissolves in concentrated sulphuric acid to form a red solution, and is stable in fairly dilute sulphuric acid, but by water is decomposed to form manganic oxide. Alums of tervalent manganese have been prepared.

Manganicyanides.—These compounds are isomorphous with the ferricyanides, and contain the ion $Mn(CN)_6'''$. *Potassium manganicyanide*, $K_3Mn(CN)_6$, is obtained in red-brown crystals by oxidizing the manganocyanide with air. Its solutions soon deposit hydrated manganic oxide.

QUADRIVALENT MANGANESE.—Compounds of quadrivalent manganese are either insoluble or contain the metal in the anion, while they all have a tendency to hydrolyse with the formation of the very stable and weakly acidic dioxide.

Manganese tetrafluoride, MnF_4, is unknown, but fluomanganites, containing the ion MnF_6'', have been prepared. *Potassium fluomanganite*, K_2MnF_6, is prepared from potassium manganate and hydrofluoric acid:

$$3MnO_4'' + 8H^. + 6F' = 2MnO_4' + MnF_6'' + 4H_2O.$$
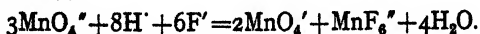
It is a powerful oxidizing agent slowly hydrolysed by water.

Solutions of manganese dioxide in cold concentrated hydrochloric acid possibly contain *hexachloro-manganous acid*, H_2MnCl_6, in addition to manganese trichloride.

Manganites.—These compounds, derived from the weakly acidic manganese dioxide, are usually made by heating manganates or permanganates to a moderate temperature. They are usually condensed substances with complex formulae, and are insoluble in water.

Manganates.—These derivatives of sexivalent manganese contain the ion MnO_4'', and are bright green. Only the sodium and potassium salts are of importance.

*2B

Potassium manganate, K_2MnO_4, is prepared by heating manganese dioxide with moist solid caustic potash in the air:

$$2MnO_2 + 4OH' + O_2 = 2MnO_4'' + 2H_2O.$$
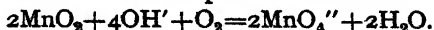
The reaction is incomplete, and the product is extracted with water and evaporated till green crystals appear. The addition of an oxidizing agent such as potassium nitrate helps the oxidation but contaminates the product. Alternatively potassium permanganate may be heated with caustic potash:

$$4MnO_4' + 4OH' = 4MnO_4'' + O_2 \uparrow + 2H_2O,$$
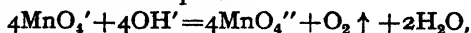
when manganese dioxide is produced at the same time by a side-reaction.

Potassium manganate is an intensely green solid isomorphous with the chromate, sulphate, and selenate. A further resemblance between these ions is the insolubility of the barium salts. On strong heating, the manganate yields a manganite and oxygen. The manganates are stable in solution only in the presence of free alkali, as the solutions otherwise turn purple and deposit manganese dioxide:

$$3MnO_4'' + 2H_2O = 2MnO_4' + MnO_2 \downarrow + 4OH'.$$

In aqueous caustic potash potassium manganate is freely soluble. The manganates are oxidizing agents.

PERMANGANATES.—Manganese heptoxide is a strongly acidic anhydride, and permanganic acid, $HMnO_4$, is a strong monobasic acid resembling perchloric acid, $HClO_4$, though its solutions are less stable. Permanganates are the final stage of oxidation of manganese compounds. On account of its high temperature-coefficient of solubility, which allows it to be easily obtained by crystallization, potassium permanganate is of much greater practical importance than the sodium salt.

Potassium permanganate, $KMnO_4$, is made on a fairly large scale from solutions of potassium manganate. In the old process the solution was acidified by passing carbon dioxide through it, but this involved the conversion of a third of the manganese to the dioxide, the starting-point of the manganate process. It is therefore more economical to oxidize the manganate solution either with chlorine:

$$2MnO_4'' + Cl_2 = 2MnO_4' + 2Cl',$$
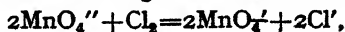
or at the anode in electrolysis, usually in a cell of diaphragm type. Potassium permanganate is also made from a manganese steel anode in aqueous caustic potash. The product is easily purified by recrystallization. It forms small crystals isomorphous with potassium perchlorate, $KClO_4$, and of a purple colour so dark as to appear nearly black. Like potassium perchlorate, it is much more soluble in hot water than in cold, but its solubility at room

temperature, about 50 gm. per litre at 12°, exceeds that of the perchlorate.

When heated above 200°, potassium permanganate yields a manganite and oxygen. The best equation is:

$$4KMnO_4 = 2K_2MnO_3 + 2MnO_2 + 3O_2 \uparrow,$$
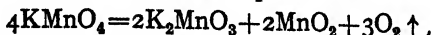
but at higher temperatures further changes take place.

Permanganates are powerful oxidizing agents of somewhat complex behaviour. The oxidation potential of the change $MnO_4' \rightarrow MnO_4''$ is 0·61 volt, so that chlorine can easily oxidize manganates to permanganates. The reverse change is of little practical significance, because in the alkaline solutions in which manganates are alone stable the reduction of permanganates proceeds further and leads to the precipitation of manganese dioxide. It is, however, possible to convert a permanganate to a manganate by boiling it with concentrated caustic alkali, or by heating the solids together, when oxygen is evolved:

$$4MnO_4' + 4OH' = 4MnO_4'' + O_2 \uparrow + 2H_2O.$$
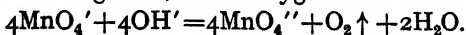
If the alkali is dilute the dioxide is precipitated instead. Usually, however, the oxidizing action of permanganate solutions follows one of two courses:

(i) in neutral or alkaline solution:

$$2MnO_4' + H_2O = 2MnO_2 \downarrow + 2OH' + 3O;$$

(ii) in acid solution:

$$2MnO_4' + 3H_2O = 2Mn^{\cdot\cdot} + 6OH' + 5O.$$
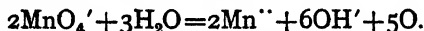
The oxidation potential of both reactions depends greatly on the hydrogen ion concentration of the solution. In a solution normal in permanganate and in acid the second change has a potential of 1·52 volts, sufficient, that is, to oxidize a chloride solution to chlorine. While these concentrations are higher than would be met with in volumetric analysis, or than stability allows, it is nevertheless imprudent to use permanganate in hydrochloric acid solution for this work, for unless the dilution is very great some permanganate may be consumed in the liberation of chlorine. Solid potassium permanganate causes a rapid evolution of chlorine from concentrated hydrochloric acid in the cold.

In volumetric analysis potassium permanganate can be used for a great variety of estimations, and on account of the intense colour of its solutions no indicator is required, though in alkaline solution the precipitated manganese dioxide is apt to obscure the end-point unless steps are taken to coagulate it at the bottom of the vessel. Permanganate solutions are affected by light, and unless kept in blue bottles suffer a slow alteration in composition; they are also easily reduced by rubber or other organic substances, so that

burettes with glass taps should be used. Among the most important oxidations with permanganate used in analysis are the following: oxalic or formic acids to carbon dioxide and water (carried out at 60°), ferrous salts to ferric salts, ferrocyanides to ferricyanides. With hydrogen peroxide in acid solution mutual reduction takes place:

$$2MnO_4' + 5H_2O_2 = 2Mn" + 5O_2 \uparrow + 6OH' + 2H_2O.$$
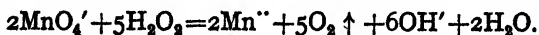
Neutral manganous solutions react with permanganate on warming to precipitate manganese dioxide:

$$2MnO_4' + 3Mn" + 2H_2O = 5MnO_2 \downarrow + 4H\dot{}.$$

This is VOLHARD's titration. To coagulate the manganese dioxide zinc sulphate is added to the liquid, whose hydrogen ion concentration also needs careful control.

Permanganates are also used in bleaching, and as antiseptics.

<div style="text-align:center">

RHENIUM

Re=186·22. *Atomic number*, 75

</div>

This rare element, discovered in 1925 in Norwegian *molybdenite*, is now extracted from spelter residues. In its valency relations it resembles manganese, though the valency of seven is more conspicious in rhenium. The density is 21·4, and the melting-point (3137°) is exceptionally high (cf. tungsten, 3370°). Like the adjacent elements tungsten and osmium, it can be made into filaments, and with its greater electrical resistance it may perhaps replace tungsten in lamps. The oxides Re_2O_3, ReO_2, ReO_3, and Re_2O_7 are known. The *heptoxide*, obtained by burning the metal, melts at 304° and can easily be distilled: it has no oxidizing properties. It is extremely soluble in water, forming a strong acid from which the colourless perrhenates are derived. These are less easily reduced than the permanganates. *Potassium perrhenate*, $KReO_4$, is slightly soluble in cold water (12 gm. per litre); sodium perrhenate is freely soluble. The *dioxide* is obtained by hydrolysis of the tetrachloride or by oxidizing the metal in oxygen at low pressure. All the oxides are easily reduced to the metal. The highest known fluoride and chloride are ReF_6 and $ReCl_5$, both made by direct combination, but rhenium forms a volatile oxychloride, ReO_3Cl, in which its valency is seven. The sulphides resemble the oxides in formula, and the *heptasulphide* Re_2S_7 is precipitated by hydrogen sulphide from strongly acid perrhenate solutions.

The volatile heptoxide and oxychloride have been used in the determination of the equivalent.

GROUP VIII

IRON, COBALT, NICKEL, RUTHENIUM, RHODIUM, PALLADIUM,
OSMIUM, IRIDIUM, PLATINUM

Fe   Co   Ni   Ru   Rh   Pd   Os   Ir   Pt

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

THE TRANSITION ELEMENTS AND GROUP VIII

IT will be seen from the diagram of the transition elements, in which
Group VIII, to which the term is sometimes restricted, is enclosed
by a dotted line, that the group differs in structure from all others
of the periodic table. Some of the physical properties of Group VIII
elements are shown in the table below; it will be observed that the
atomic weights of cobalt and nickel lie out of order (p. 318).

	Fe	*Co*	*Ni*	*Ru*	*Rh*	*Pd*	*Os*	*Ir*	*Pt*
Atomic Number	26	27	28	44	45	46	76	77	78
Atomic Weight	55·85	58·94	58·71	101·1	102·91	106·4	190·2	192·2	195·09
Density (max.)	7·86	8·8	8·8	12	12	12	24	22·4	21·7
Atomic Volume	7·1	6·7	6·7	8·5	8·6	8·9	8·0	8·6	9·0
Melting-point	1533°	1480°	1450°	1950°	1966°	1550°	2500°	2454°	1774°

SOME PHYSICAL PROPERTIES OF GROUP VIII ELEMENTS

These elements are all metals of high melting-point, arranged in
three characteristic 'triads.' Since they bear a marked relation-
ship not only to each other but to the adjacent transition elements,
it will be convenient to consider here one or two characteristics
of the group as a whole. The atomic volumes of the transition
elements and of the elements in the B subgroups of Groups I and II
are shown in Fig. 146, from which it will be seen that the Group VIII
elements all have similar values between 6·7 and 9·0 and occupy
minima in the series.

The electronic structure of the atoms of the 18 elements between K ($Z=19$) and Kr ($Z=36$) inclusive results from the filling of the electron group IV (cf. diagram on p. 347), after the completion of the argon core (2, 8, 8) in the preceding lighter elements. Experimental spectroscopic evidence, as well as modern theory of atomic
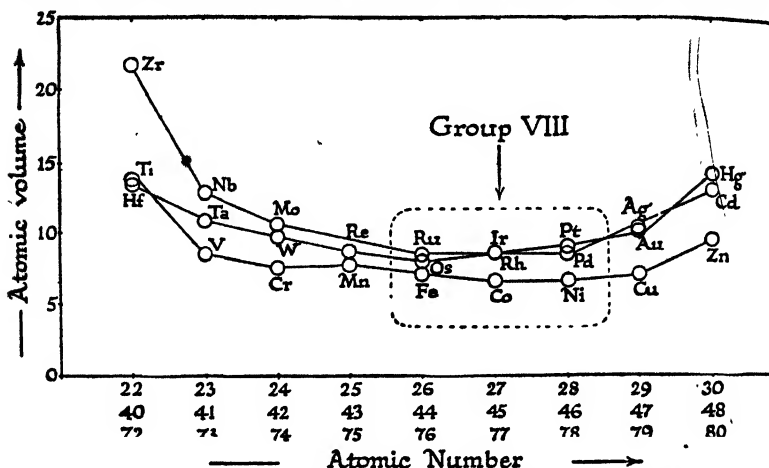
FIG. 146   ATOMIC VOLUMES OF THE TRANSITION ELEMENTS

structure, show that this fourth electronic group is composite, and can be subdivided into three subgroups, which, following the spectroscopic nomenclature ($4s$, $3d$, and $4p$), we shall call s, d, and p. The maximum electronic contents are: s, 2; d, 10; p, 6, making 18 in all for the whole group. The bonding energies of the electrons in the three subgroups are similar, justifying their inclusion in one main group. The detailed order of filling of the subgroups, which is not quite regular, is shown in the following table:

	Element			Maximum Valency
19	K	1	—	1
20	Ca	2	—	2
21̄	Sc	2	1	3
22	Ti	2	2	4
23	V	2	3	5
24	Cr	1	5	6
25	Mn	2	5	7
26	Fe	2	6 (5+1)	3 (6)
27	Co	2	7 (6+1)	3
28	Ni	2	8 (7+1)	3 (?)
29	Cu	1	10 (9+1)	2
30	Zn	2	10	2

Up to and including Mn all the electrons in both subgroups s and d contribute to the maximum valency. When, however, the subgroup d is half-filled, i.e. at Fe, most of its electrons abruptly cease to be available for valency purposes, and the production of stable compounds. From Fe onwards only one of the electrons from subgroup d is so used, as is indicated by the parentheses in the table. In the unstable ferrates (p. 785) iron is probably sexivalent, and we see the vestiges of the use of more than one electron from subgroup d. The six elements from Ga ($Z=31$) to Kr ($Z=36$) are formed by the filling of the subgroup p, which remains empty until Ga is reached. The similarity in the bonding energies of electrons in subgroups s and d is responsible for the very variable valencies of the elements from Ti to Mn, for the valency actually exerted will depend mainly on whether the chemical environment of the atom is reducing (tending to add electrons) or oxidizing (tending to remove electrons).

The transition elements are all metals, usually with high melting-points, of variable valency. Their compounds are usually coloured, and they have the high catalytic activity associated with variable valency. In Group VIII the metals, with the exception of iron, are all noticeably resistant to oxidation or chemical attack. Iron, cobalt, and nickel are more electropositive than the rest, and also more abundant. The great abundance of iron and its comparative susceptibility to corrosion mark it out from the rest. Excluding these three metals, it will be noticed that the remainder are all scarce and negligibly electropositive (low atomic volume). Consequently most of their halides are insoluble in water (compare silver and gold), or dissolve in it to form complexes with the metal in the anion.

The valencies throughout the group are very variable, and the study of the compounds of these elements is a fascinating but complicated problem. They may be classified either horizontally or vertically; we shall adopt the horizontal classification, but frequent allusion will be made to vertical comparisons. Higher valencies become more marked as we move from right to left or from top to bottom; thus nickel is seldom other than bivalent, while osmium displays the highest valency—eight—of any element in a binary compound. Throughout the group the stability of various valencies depends greatly on complex formation, for which all Group VIII elements have a conspicuous aptitude. Several complexes will be discussed later on, but we may mention here the complex bivalent cations which the first long-period elements form with ammonia, which increase in stability from iron to copper, and the very important complex cyanides. With the elements of the iron column the most stable complex cyanide ions are those in

which the metal has an electrovalency of two—e.g. the ferrocyanides, $Fe(CN)_6''''$; with the cobalt column elements the cobalticyanides, $Co(CN)_6'''$, containing the tervalent metal, may be taken as typical; while with the nickel column the metal is bivalent again—e.g. the platinocyanides, $Pt(CN)_4''$. The study of the complex halides is also interesting, but rather less simple. Cobalt, rhodium, iridium, and platinum, and to a less degree the other elements of the group, are remarkable for the number and stability of their complex ammines.

IRON

Fe $=55·85$. *Atomic Number*, 26

History.—Iron may have been an Asiatic discovery. It was certainly known in Asia Minor about 1300 B.C., for one of the kings of the Hittites presented an iron sword to the celebrated Pharaoh of the Nineteenth Dynasty, RAMESES II. An iron tool was also found embedded in the masonry of the Great Pyramid at Gizeh, thus presumably dating from about 2900 B.C., when the pyramid was being built. Ancient names for iron are usually to be interpreted as 'the celestial metal' or 'the metal from heaven,' indicating that the first known specimens were of meteoric origin. By the time of SOLOMON, the extraction of iron from its ores must have been well established, since about 2500 tons of the metal were used in the construction of his temple at Jerusalem. We read, too, that NEBUCHADREZZAR (about 600 B.C.) carried off into captivity a thousand iron-workers from Damascus.

Certain specimens of ancient Egyptian iron, when subjected to chemical analysis, were found to contain combined carbon, which suggests that they may have been made of steel. Case-hardening, for steel tools, is definitely known to have been in use in the seventh century B.C., while the Indian steel employed for the celebrated Yemen blades was probably imported to Arabia as early as the fourth or fifth century B.C.

The word 'iron' is of Anglo-Saxon origin. Among the alchemists, the metal was known as Mars, from its supposed astrological connection with the planet.

Occurrence and Extraction.—Iron is the most abundant of the metals, with the single exception of aluminium, but the great difficulties which attend the extraction of aluminium, and which have been overcome only in recent years and in the treatment of selected ores, have caused iron to be incomparably the more useful. Iron occurs principally as oxide or sulphide, but sulphide ores cannot conveniently be used for iron manufacture, though they are much used for making sulphur dioxide. The principal oxide

ores are *haematite*, Fe_2O_3; *limonite*, hydrated Fe_2O_3; and *magnetite*, Fe_3O_4. They occur in many parts of the world, some of the richest deposits being in the United States, Great Britain, Scandinavia, Belgium, Alsace-Lorraine, Germany, China, and Brazil. Not all of these, however, are worked, for the value of an iron ore depends on many factors besides its iron content, which should be at least 30 per cent. Cheap transport and cheap coal are essential, magnetite requiring more fuel than the other ores. The physical properties of the ore are important, as a powdery ore cannot be worked in a blast furnace without preliminary treatment. The nature of the impurities must also be considered, as the presence of silicates, phosphorus, sulphur, or limestone will influence the extraction process. The presence of coal and iron in adjacent dis-

FIG. 147. BLAST FURNACE

tricts was one of the principal reasons for the industrial supremacy of Great Britain in the nineteenth century.

The manufacture of iron by heating its oxide ores with carbon has been carried out since the beginnings of history, though the general use of iron was preceded by that of copper and bronze. In modern times the operation is carried out in a blast furnace. This is a firebrick tower cased in iron which may be one hundred feet high: it is fed with the ore mixed with coke and a flux to enable the impurities in the ore to form a liquid which can be withdrawn from the furnace. The nature of the flux depends on the impurities present: if there is much lime an acidic flux like silica is added, if much silica, a basic flux like lime, so that the slag usually consists largely of calcium silicate.
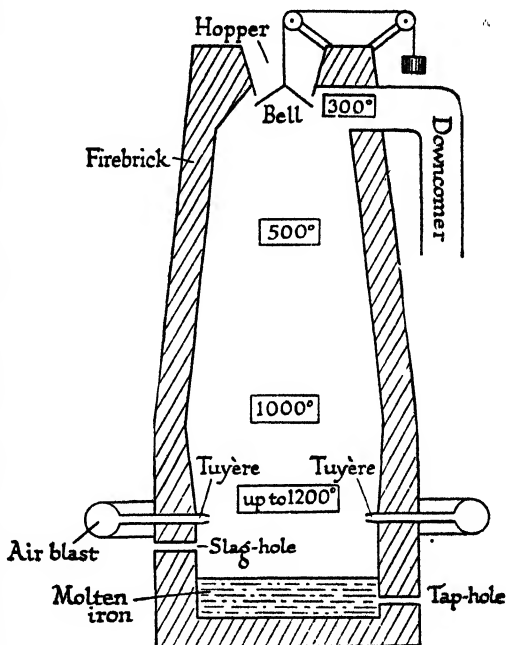
The air required for the combustion of the coke is fed in near the bottom of the furnace through pipes, called *tuyères*, or ' twyers,' which project slightly into the interior. Just below the tuyères is the slag-hole, though which the slag is discharged, and lower still is the tap-hole from which the molten metal is run whenever the level inside reaches nearly to the slag-hole. One of the greatest advances in the art of making iron was begun in 1828, when NEILSON heated the air-blast before admitting it to the furnace. The heat of the furnace gases, which leave the furnace by a pipe called the 'down-comer,' is generally employed for the purpose. These gases contain a considerable proportion (about 24 per cent) of carbon monoxide, and are burned, with the help of a further air-supply, in a tower provided inside with a brick chequer-work to absorb as much as possible of the liberated heat. When the temperature within this tower is sufficiently high, the furnace gases are deflected into another similar structure and the air-blast is heated by passing it through the hot tower. In modern practice the furnace gases are used not only to heat the air-blast but to raise steam for power, and are even burned in combustion-engines for the same purpose. Progress has been made since the days when the gases burning at the open mouths of the furnaces lighted up the night countryside for miles around.

The essential reaction in the furnace is the reduction of the iron oxides by carbon monoxide, e.g.:

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2.$$
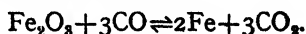
Since the reaction is reversible, and since it is important to ensure complete reduction of the ore, conditions have to be such that the carbon monoxide is in considerable excess. Hence the presence of such a high proportion of the monoxide in the gases that leave the furnace.

The heat required to raise the mass to the necessary high temperature for this reaction is supplied by the heat of formation of the carbon monoxide from the coke and the hot air-blast. The process is continuous, and a furnace once lit need not be interrupted until the lining is worn out. The temperature in the neighbourhood of the tuyères, where the metal is being melted, may reach 1200°, but higher up the furnace the temperature falls and the issuing gases are at about 300°.

The product of the blast furnace is called *cast iron*, or sometimes *pig iron*, from the ' pigs ' or ingots made by running it into moulds. It contains some 5 per cent of impurity, mostly carbon, but phosphorus, silicon, and sulphur are also usually present. Large quantities of cast iron are used without further purification. As its name implies, it can be used for making casts, since it expands on solidification, but it is brittle, cannot be welded, and will not

sustain heavy loads. These difficulties can be overcome by the use of wrought iron or steel.

Wrought iron is simply cast iron from which the impurities, particularly the carbon, have been almost entirely removed. Wrought iron is tough, and before the invention of the BESSEMER process for making steel was of much greater importance than it is now. It is made by heating cast iron to a very high temperature with iron ore in a reverberatory furnace, such as that shown in the diagram. In this furnace the heat is reflected from the roof and sides, and the carbon and other impurities in the cast iron are slowly
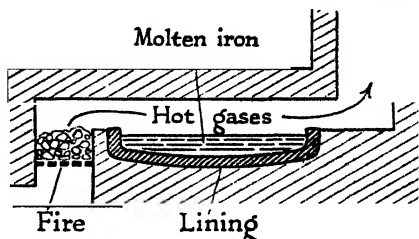
FIG. 148. REVERBERATORY FURNACE

oxidized by the oxygen of the ore. As the carbon is removed the melting-point of the iron rises and the metal, at first liquid, begins to 'ball together' or solidify. It is stirred with long poles called 'rabbles' inserted through an opening in the wall of the furnace not shown in the diagram. This operation, called 'puddling,' is still carried out by hand, and the iron is finally removed from the furnace on the end of these poles: it is immediately placed under a steam hammer and, while still hot, squeezed free from slag.
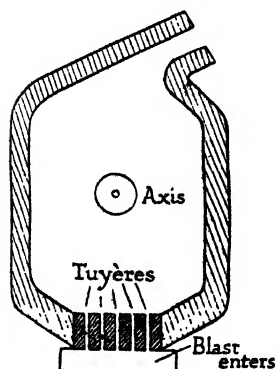
FIG. 149. BESSEMER CONVERTER

Before the invention of the Bessemer converter in 1855 steel was made from wrought iron and carbon by a laborious process which, moreover, on account of the very high temperature required, could be applied only to small masses of metal at a time. Bessemer conceived the idea of rapidly oxidizing the carbon and other impurities in molten cast iron by blowing air through it, thus eliminating the puddling and subsequent processes. The vessel in which the oxidation is carried out is called a converter; modern examples are twenty or thirty feet high and have an internal diameter of about eight feet, holding thirty tons of metal. The first converters were fixed, but modern converters can be tilted about a horizontal axis. They are filled with the tuyères horizontal and the curved outlet pointing upwards; the molten iron is poured into it from a travelling ladle. The converter is then turned into the

position shown in the diagram and the air-blast is turned on at an excess pressure of some two atmospheres. The carbon is oxidized to carbon monoxide, which burns at the mouth of the converter, and other impurities are also removed as volatile oxides. In the earlier forms of the process phosphorus could not be removed, and it was necessary to work with ores which contained none. It was, however, discovered that with a dolomite lining and a blast of more than usual duration a metal quite free from phosphorus resulted; this is called the 'basic Bessemer process.' HOOD, in his book *Iron*, tells the story of how the possibility of using a dolomite lining was discovered in 1878 by THOMAS, clerk to the magistrates at the Thames police court, who had taken up the study of chemistry as a hobby, and who had had no practical experience whatever of the iron trade.
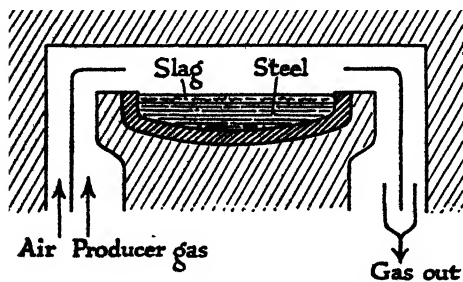
FIG. 150.   SIEMENS OPEN-HEARTH FURNACE

The product of the process is tipped out of the converter, and is now called *steel*. Before the introduction of the converter the term 'steel' was applied to wrought iron to which some 2 per cent of carbon had been added. Modern steels may contain less carbon even than wrought iron, the term referring simply to metal which has been prepared in a converter or by the alternative processes. The proportion of carbon left in the iron depends on the duration of the blast. Bessemer found that if the blast was continued long enough to remove all the carbon, some of the iron was oxidized as well, and this quite spoiled its properties. Soon, however, the discovery was made that if manganese was added, nearly all the carbon could be oxidized without any oxidation of the iron, and this discovery contributed much to the supremacy which the Bessemer process so long enjoyed. That process, however, is by some now considered to be obsolescent, and is menaced on the one hand by the SIEMENS open-hearth process and on the other by the electric furnace.

The open-hearth steel furnace was introduced at a comparatively early date. Cast iron is melted with ore and a flux, usually lime, on a lining which may be either silica or dolomite, the source of heat being burning pre-heated producer-gas. An intensive system of heat regeneration is required to reach the high temperature necessary, and is an essential part of the plant. The furnace is

sometimes made reversible; that is to say, the air and producer-gas are led into it through brick chequer-work which has just been heated by the issuing gases. The open-hearth furnace differs from the simple reverberatory type in the source of heat, the provision of a heat-regeneration system, and the use of a flux. This flux forms a slag which floats on the surface of the steel and protects it from the oxidation which would otherwise take place. The manufacture of steel in this furnace takes longer than in the Bessemer converter, but it is more easily controlled and the product is more uniform in composition. The addition of deoxidizers such as ferro-manganese, ferro-titanium, or aluminium scrap effects a great improvement in the quality of the steel.

The electric furnace has been applied to steel manufacture in comparatively recent times, and its use is said to be increasing. Several types are in existence, the current being usually conveyed to the metal by carbon electrodes. The chief advantage of all such furnaces is the very high temperature that can be reached.

Carbon-containing steels contain the carbon partly as *cementite*, a carbide of iron with the formula Fe_3C. The heat treatment of steel is intimately connected with the changes undergone by iron on heating or cooling, and belongs to the science of metallurgy rather than to pure chemistry.

Special Steels.—The greatest development of modern metallurgy has been in the production of alloys. Modern high-speed machinery, particularly of the reciprocating type, requires metals of great toughness, tensile strength, and resistance to wear, and the manufacture of special steels for these purposes has become an industry of the highest importance. Some special steels are mentioned below, others in connection with the metals that they contain.

Steel for High-speed Tools.—This steel must be capable of standing high temperatures without softening. A typical specimen contains: tungsten 15 per cent, chromium 4 per cent, vanadium 1 per cent. The tungsten is sometimes replaced by molybdenum in smaller quantity. The steel is heated to about 1300° and quenched in oil.

Steel for Constructional Work, e.g. bridges.—The necessary strength is obtained by the use of 3 per cent nickel, 1 per cent chromium, and sometimes small quantities of manganese and vanadium. Such steels are also used for the frames of motor cars.

Steel for specially Hard Wear.—For the jaws of rock-crushers, for rails on sharp curves, for steel helmets, and for similar purposes, a steel containing about 10 per cent of manganese is used.

Stainless Steel.—This is used for cutlery. It contains 12 per cent of chromium.

Steel for Reciprocating Machinery.—These steels contain chromium and vanadium in very variable proportions.

Steel for Permanent Magnets.—Such a steel may contain 30 per cent of cobalt. Stainless steel is also suitable for the purpose.

Properties.—The physical and even the chemical properties of iron are profoundly modified by the small quantities of carbon and of other impurities which the commercial substance usually contains, and the product of large-scale metallurgical operations is not suitable for the investigation of the properties of the pure element. This is best prepared either electrolytically or by reducing in a current of hydrogen any oxide of iron, or such a salt as ferrous chloride. For electrolysis ferrous sulphate may be used in the bath, but the hydrogen ion concentration must be carefully controlled. In strongly acid solution hydrogen is produced, and even a slightly acid solution might lead to occlusion of hydrogen in the cathode, while excess of hydroxyl ions produces a precipitate of ferrous hydroxide. The bath is therefore buffered by the addition of magnesium sulphate, which precipitates magnesium hydroxide in alkaline solution, and sodium hydrogen carbonate, which prevents any accumulation of hydrogen ions. Oxidation by the air must be avoided by carrying out the electrolysis in an atmosphere of carbon dioxide, or by leaving intact the layer of ferric hydroxide which collects on the surface of the liquid if the operation is carried out in the air. The anode is made of wrought iron, and the cathode, which is kept in rotation, of platinum or copper.

Pure iron has properties very different from those of the commercially more important alloys which may differ from it only slightly in chemical composition. It is a white metal which melts at 1533° and boils at 3235°. The density is 7·9, and the metal is soft, ductile, and malleable; it can be obtained in the form of fairly large crystals, but this is not easy. Solid iron exists in three, or possibly four, allotropic modifications, the stability ranges being as follows: α-, up to 769°; β-, 769° to 928°; γ-, 928° to 1404°; δ-, 1404° to melting-point. Of the transition-points that at 928° is the most conspicuous, and the transformation of γ- to β-iron gives out so much heat that a wire which has been strongly heated and then allowed to cool slightly below the temperature of redness suddenly glows brightly as the transition temperature is reached, a phenomenon to which the name 'recalescence' has been given. Most of the physical properties of pure iron show a discontinuity at this temperature. X-ray examination has shown that the transition from β-iron to γ-iron is accompanied by a change in the crystal structure.

Like many other metals, iron is permeable to hydrogen, and under suitable conditions will occlude quite large volumes of the gas. Nascent hydrogen will pass through sheet iron even at ordinary temperatures, and ordinary hydrogen will pass through the metal

at higher temperatures, say 800° or over. This has caused serious difficulty in plants in which hydrogen at high pressures and temperatures has to be kept in iron vessels—e.g. in factories working the HABER-BOSCH process.

Since the standard electrode potential of iron is −0·44 volt, it will not dissolve to any appreciable extent in pure cold water. In the presence of oxygen and water iron is, however, more or less rapidly corroded, with the formation of a loose brown mass of hydrated ferric oxide, called ' iron rust.' It can be shown experimentally that neither pure water nor pure oxygen is alone sufficient to cause corrosion, but it is still an open question whether iron will rust in aerated water from which all traces of carbon dioxide have been excluded. Experiments in which the surface of the metal and the apparatus are washed with alkaline solutions are inconclusive, since it is definitely known that iron will not rust under caustic alkalis. A certain concentration of ferrous ions in the solution is presumably necessary to the formation of rust, and since the solubility of iron in aqueous solutions depends chiefly on their hydrogen ion concentration, it is not surprising that the metal should remain untarnished under caustic alkalis. There is, however, no doubt that the increase in the hydrogen ion concentration brought about by the presence of carbon dioxide causes the attack on the metal to be much more rapid in natural fresh water than in pure distilled water containing air but free from carbon dioxide.

Many metals, such as aluminium (standard electrode potential −1·66 volts) or zinc (−0·76 volt), which are more electropositive than iron, are yet far more resistant to the action of water. The explanation is probably that iron rust is a porous substance which offers no protection to the metal beneath it, while the oxides of aluminium or zinc, when present in quantities so small as to be invisible to the eye, form a coherent coating which prevents any further attack.

Iron is readily soluble in dilute acids, with the formation of ferrous salts and hydrogen. The marked odour of the gas obtained from acids and commercial iron must be attributed to impurities in the metal, and is altogether absent if the purest iron is used. Even faintly acid solutions—e.g. solutions of ammonium salts—will dissolve iron without difficulty. The action of nitric acid is very complicated. If the acid is extremely dilute, ferrous nitrate is formed and some of the nitric acid is reduced to ammonia, which forms ammonium nitrate. No gas is therefore evolved:

$$4Fe + 10H^{\cdot} + NO_3{'} = 4Fe^{\cdot\cdot} + NH_4{'} + 3H_2O.$$
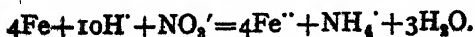
As the acid grows rather more concentrated, ferric nitrate is the principal product, and gas is evolved; with acids of various concentration,

nitrous oxide, nitric oxide, nitrogen dioxide, and ammonium salts may all be produced in varying proportions. Concentrated nitric acid has no action on iron, which when placed in this liquid is said to become 'passive.' It has already been explained (p. 423) that this is due to a skin of oxide which covers the metal. Iron is unaffected by cold alkaline solutions, which protect it from corrosion, but it is attacked by boiling concentrated alkaline solutions, or by fused caustic alkali.

Pure dry oxygen begins to attack iron at about 150°. At first the action is limited to the production of very thin films of oxide which produce interference-colours on the surface of the metal. These colours are used by workmen to estimate the temperatures reached during the heat treatment of steel. If heated to a high temperature in oxygen, iron can be made to burn, but the temperature necessary depends chiefly on the state of subdivision. Iron wire or iron gauze will burn in oxygen if ignited with burning sulphur, or even in air if heated in a Bunsen flame, while the iron powder obtained by reducing iron compounds in hydrogen is pyrophoric at ordinary temperatures. All forms of iron will reduce steam with the production of ferrosoferric oxide:

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2,$$
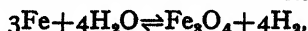
and though the equilibrium can be but little affected by the physical condition of the metal, yet the rapidity with which equilibrium is reached is greatly influenced by this factor: iron powder reacts on gentle warming, whereas iron lumps show no measurable action below 300° or 400°.

Iron reacts with the halogens when gently heated with them, and is strongly corroded by chlorine at the ordinary temperature.

OXIDES AND HYDROXIDES.—In addition to ferrous oxide, FeO, and ferric oxide, Fe_2O_3, an oxide of intermediate formula, Fe_3O_4, is known. All these oxides can be obtained in the hydrated state.

Ferrous oxide, FeO, can be obtained only with difficulty in a state of purity, as it is easily reduced to the metal or oxidized to ferric oxide or ferrosoferric oxide. It can be prepared by careful oxidation of the metal—e.g. by exposing the amalgam for some time to the air—or by reducing ferric oxide with pure carbon monoxide at a temperature which must not rise much above 500°. The ignition of ferrous oxalate in an inert atmosphere yields a pyrophoric mixture of iron and ferrous oxide.

The properties of the oxide depend on its state of division. If finely powdered it will burn readily in the air and decompose boiling water, liberating hydrogen and forming ferric hydroxide:

$$2FeO + 4H_2O = 2Fe(OH)_3 + H_2 \uparrow.$$
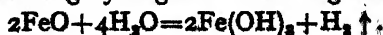
is soluble in acids.

Ferrous hydroxide, $Fe(OH)_2$, is obtained as a colourless precipitate by the addition of caustic alkalis to ferrous solutions. As it is rapidly oxidized by the air, turning first green then brown, it must be prepared in an inert atmosphere and with solutions from which all dissolved air has been removed. Oxidation proceeds so vigorously that if exposed to the air the hydroxide may become incandescent. Like ferrous oxide, it is soluble in acids and will liberate hydrogen from boiling water. Unlike ferric hydroxide, ferrous hydroxide is a strong base without amphoteric properties.

Ferric oxide, Fe_2O_3, occurs plentifully in nature as haematite or specular iron ore. In the laboratory it can be prepared by heating the easily obtained ferric hydroxide, or by roasting almost any compound of iron in air or oxygen. Iron pyrites is used for this purpose on a very large scale in the manufacture of sulphur dioxide, though its place has in recent years been partly taken by American sulphur. The reaction is:

$$4FeS_2 + 11O_2 = 8SO_2 + 2Fe_2O_3,$$
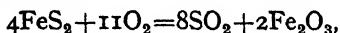
and the residue of ferric oxide is used as a source of other iron compounds, as a catalyst, or in smaller quantities as a red pigment.

Ferric oxide is a red substance which melts at 1565° and dissolves only with difficulty in acids. Its magnetic properties are very weak. It can be reduced to the metal with hydrogen, or by carbon monoxide at high temperatures, but at 500° carbon monoxide produces ferrous oxide. When very strongly heated, ferric oxide loses oxygen and forms ferrosoferric oxide, Fe_3O_4. It was formerly used as a catalyst in the contact process for sulphuric acid, with cupric oxide as promoter, but it has now been largely superseded by vanadium compounds. Ferric oxide also catalyses the reaction between carbon monoxide and steam, now of technical importance:

$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$

Ferric hydroxide, $Fe(OH)_3$, is produced as a brown precipitate when caustic alkalis are mixed with cold ferric solutions. By prolonged boiling, a red compound with the composition $Fe_2O_3.H_2O$ is obtained. Both these substances readily dissolve in acids to form solutions of ferric salts. Ferric hydroxide so readily adsorbs substances from the solutions in which it is precipitated, and retains them with such tenacity during washing, that it is best to use the volatile precipitant aqueous ammonia, which can be expelled from the product by heating. Ferric hydroxide is easily obtained in colloidal solution. It is a weak base and is produced by the hydrolysis of ferric salts; thus if a few drops of a solution of ferric chloride are added to a large volume of boiling distilled water, a deeply coloured yellow, brown, or red solution is obtained from

which hydrogen chloride can be removed by dialysis. When prepared in this way, ferric hydroxide is a positively-charged colloid easily coagulated by electrolytes, particularly those containing multivalent anions such as sulphates, but it can also be prepared as a negative colloid.

The precipitation of ferrous and of ferric hydroxide is prevented by the addition of certain hydroxylic substances, such as glycerol or tartaric acid, with which the ferrous and ferric ions form complexes (compare aluminium). The precipitation of ferrous hydroxide with ammonia is also prevented by the presence of excess of ammonium salt, which represses the dissociation of the base. Ferrous ions form a complex $(Fe.6NH_3)^{..}$ with ammonia, but no corresponding complex of ferric ions is known.

Ferrites.—These substances are derivatives of ferric iron, not of ferrous iron, as the name might suggest, and may contain the ion FeO_2'. They are obtained by heating ferric oxide with another metallic oxide or hydroxide, e.g.:

$$Fe_2O_3 + 2NaOH = 2NaFeO_2 + H_2O,$$
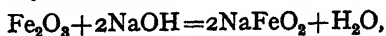
or by adding caustic alkali to a mixed solution of a ferric and another salt and igniting the hydroxide precipitate so obtained. The ferrites are either insoluble in water or, like sodium ferrite, decomposed by it into the constituent bases. Sodium ferrite is used in one process for the manufacture of caustic soda (p. 439). The hydrated ferric oxide obtained by the decomposition of this substance has the composition $FeO(OH)$, or $Fe_2O_3.H_2O$, identical in constitution with the mineral *goethite*. Sodium ferrite can, however, exist in concentrated alkaline solution, and is usually prepared by heating ferric oxide with concentrated caustic soda.

Ferrosoferric oxide, Fe_3O_4, can be prepared by heating the precipitate which caustic soda produces in mixed ferrous and ferric solutions. It is a black solid, melting at 1527°, which occurs in large quantities in nature as the mineral *magnetite*. It is the most stable oxide of iron at very high temperatures, and may be prepared by heating ferric oxide to 1500° or over. It is also produced by the balanced action between iron and steam, or by burning iron in oxygen, but if subjected to prolonged heating in air or oxygen at about 1300° it is converted to ferric oxide.

It is much more strongly magnetic than the other oxides of iron, and in the natural form has been called 'lodestone'; it is also known as *magnetic oxide of iron*. Although composed of the simple ions $Fe^{..}$, $Fe^{...}$, and O'', the oxide is insoluble in dilute acids and dissolves only slowly in concentrated acids to give a mixed ferrous and ferric soution. The action of caustic alkali on such a solution produces a precipitate which has the formula $2Fe_3O_4.3H_2O$, and

from which the water can be removed by heating. This precipitate is soluble in acids, and from the solutions salts such as $Fe_2Cl_6.18H_2O$ can be obtained. They are probably complex salts, e.g. $Fe(FeCl_4)_2$.

Ferrates, which contain the anion FeO_4'', may be regarded as derivatives of the unknown iron trioxide, FeO_3. They are more stable than the ferrites, since solutions of the soluble ferrates (e.g. those of the alkali-metals) can be kept for several days, and the insoluble barium ferrate can be boiled with water without decomposition. They are, however, decomposed even by the most dilute acids, yielding a ferric salt and oxygen or an oxidation-product of the acid anion—e.g. chlorine from hydrochloric acid. Ferrate solutions are deep red in colour.

Potassium ferrate, K_2FeO_4, is prepared by the action of oxidizing agents such as ozone, chlorine, bromine, or hypochlorites on a suspension of ferric hydroxide in aqueous caustic potash:

$$2Fe(OH)_3 + 4OH' + 3O = 2FeO_4'' + 5H_2O.$$
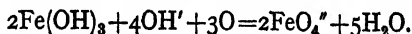
The solid salt can be obtained by cooling the solution: it forms black crystals which are isomorphous with potassium sulphate or potassium chromate. *Sodium ferrate,* Na_2FeO_4, can be prepared in a similar fashion, or by heating ferric oxide with sodium peroxide and extracting the product with water. *Barium ferrate,* $BaFeO_4.H_2O$, is obtained as a purple precipitate by the action of soluble ferrates on barium solutions.

It is somewhat surprising in view of the relative stability of chromates and permanganates, in which the metals immediately preceding iron display their highest valencies of six and seven respectively, that ferrates, in which iron exhibits a sexivalency, should be so unstable. The cause of this abrupt change may lie in the stability of the half-filled $3d$ group of electrons, which is reached in manganese (see also p. 773).

Nitrides.—Of the various nitrides of iron which have been described, the most important has the formula Fe_2N. It is a grey solid prepared by heating either the metal or ferrous chloride or bromide in a current of ammonia, and when strongly heated decomposes into its elements. If heated in hydrogen the nitride undergoes a reversible reaction:

$$2Fe_2N + 3H_2 \rightleftharpoons 2NH_3 + 4Fe.$$
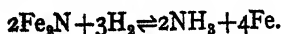
It is readily soluble in acids, from which it liberates hydrogen, leaving a ferrous and an ammonium salt:

$$2Fe_2N + 10H' = 2NH_4^{\cdot} + 4Fe^{\cdot\cdot} + H_2 \uparrow.$$

The formulae of Fe_2N and Fe_4N, which latter is formed by heating Fe_2N to 600°, have been confirmed by X-ray analysis.

It has recently been discovered that certain steels can be given a very hard surface simply by heating them to 500° in ammonia. The hardness is due to a thin coating of the nitride.

Salts of Iron.—Iron forms two series of salts, the ferrous salts, in which it is bivalent, and the ferric salts, in which it is tervalent.

FERROUS SALTS.—The action of acids on iron always produces ferrous solutions, unless the acid is an oxidizing agent, or unless oxidation by the air takes place. Ferrous salts are also easily prepared by reduction of ferric salts with iron or any other suitable reducing agent. They are isomorphous with the salts of many other bivalent metals, such as cobalt, nickel, copper, magnesium, calcium, zinc, cadmium, chromium, or manganese. Their solutions are practically colourless, and any green tinge indicates the presence of ferric salt. Unlike ferric hydroxide, ferrous hydroxide is a strong base, and ferrous solutions are scarcely hydrolysed. The carbonate, oxalate, sulphide, and phosphate are insoluble in addition to the hydroxide. The ferrous ion forms a not very stable complex ion $(Fe.6NH_3)^{\cdot\cdot}$ with ammonia, and an exceedingly stable complex with cyanides—the ferrocyanide ion, $Fe(CN)_6''''$. It also forms complexes with many hydroxylic organic compounds. The complex ion $Fe(C_2O_4)_2''$ which the ferrous ion forms with oxalates has probably the chelate structure:

$$
\begin{array}{c}
CO\!-\!O \diagdown \qquad \diagup O\!-\!CO \\
\qquad\quad >\!Fe\!<\qquad\quad \\
CO\!-\!O \diagup \qquad \diagdown O\!-\!CO
\end{array}
$$

With dimethylglyoxime ferrous solutions produce a pink colour: this is a very sensitive test for the metal.

Simple ferrous compounds are strongly paramagnetic, but complexes containing ferrous iron such as the ferrocyanides are diamagnetic.

FERRIC SALTS are prepared by the action of oxidizing agents on iron or on ferrous salts. The hydroxide is a weak base, and the hydrolysis of ferric solutions is considerable. As ferric hydroxide is extremely insoluble in water, the hydrolysis is an irreversible process and varies with the age of the solution, so that in measuring it it is difficult to get concordant results. At 25°, a solution of a ferric salt of a strong acid is 50 per cent hydrolysed at a dilution of about M/100; ferric solutions are much more hydrolysed than aluminium solutions under similar conditions of dilution and temperature. The ferric ion is colourless in solution or possibly faintly violet, but this colour is to be seen only in acid solutions of the salts of the strong oxyacids, such as the sulphate, nitrate, or perchlorate. Other solutions have the yellow or brown colour of the colloidal ferric hydroxide produced by hydrolysis; this colour

usually becomes deeper with age, but is diminished by addition of the strong oxyacids. In the solid state anhydrous ferric salts are colourless, yellow, or brown.

Some ferric salts, such as the chloride or bromide, resemble the corresponding compounds of aluminium in being chiefly covalent. The ferric ion has a very noticeable tendency to complex formation, which, if we exclude the ferrocyanides, is much less conspicuous in the ferrous ion. It does not appear to form any complex with ammonia, but with cyanides it produces the exceedingly stable ferricyanide ion, $Fe(CN)_6'''$, with fluorides the very stable ion, FeF_6''', and also forms various stable anions with pyrophosphates and orthophosphates, as well as complexes, probably chelate in character, with hydroxylic organic compounds such as mannite.

The principal insoluble salts, in addition to basic salts, are the sulphide, orthophosphate, and arsenate.

THE FERROUS-FERRIC EQUILIBRIUM.—The oxidation potential of the change $Fe'''{\rightarrow}Fe''$ is 0·77 volt. Ferrous solutions can be oxidized by the air according to the equation:

$$4Fe'' + O_2 + 2H_2O = 4Fe''' + 4OH',$$
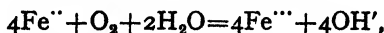
but at room temperature and in neutral or slightly acid solution the velocity of the reaction is negligible. It is probably a heterogeneous reaction which takes place on the walls of the vessel, and it can be catalysed or 'induced' by the simultaneous atmospheric oxidation of arsenites, phosphites, or other reducing agents. It is accelerated by strong acids, and still more so by alkalis. The reduction of ferric solutions is also easy, and can be carried out with copper or any less electronegative metal, or even by shaking the solution with charcoal. Finely-divided iron, sulphur dioxide, hydrogen sulphide, and stannous chloride are other reducing agents frequently employed. Oxidations by ferric ions are often sensitive to light.

The powerful reducing properties of ferrous salts in alkaline solution—that is, of ferrous hydroxide—are due to the extreme insolubility of ferric hydroxide, whose solubility-product is 10^{-36}, as compared with 10^{-14} for ferrous hydroxide. The equilibrium:

$$4Fe(OH)_2 \downarrow + O_2 + 2H_2O \rightleftharpoons 4Fe(OH)_3 \downarrow$$
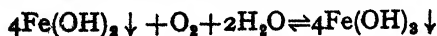
is therefore overwhelmingly in favour of the ferric compound. The equilibrium between ferrous and ferric ions is also greatly modified if anions are present with which ferric ions form complexes—e.g. fluorides or phosphates. As these considerations are of fundamental importance in the chemistry of iron, some examples will be given of the ferrous-ferric equilibrium in various media:

Hydrogen.—In the absence of a catalyst ferric solutions are

reduced by gaseous hydrogen only with extreme slowness, but in the presence of platinum or palladium the action is fairly rapid:

$$2Fe^{...}+H_2 \rightarrow 2Fe^{..}+2H^{.}.$$

Ferrous hydroxide, however, can be made to reduce water to hydrogen (palladium chloride catalyst):

$$2Fe(OH)_2 \downarrow +2H_2O \rightarrow 2Fe(OH)_3 \downarrow +H_2 \uparrow.$$
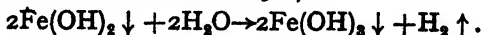
Nitrates.—Ferrous salts are not oxidized by nitrates in cold neutral solution, but ferrous hydroxide will reduce nitrates to ammonia.

Iodides.—The standard electrode potential of iodine, $+0.54$ volt, is less than the ferric-ferrous oxidation potential, so iodides are almost quantitatively oxidized by ferric salts to iodine:

$$2Fe^{...}+2I' \rightarrow 2Fe^{..}+I_2.$$
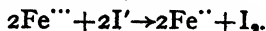
The reaction is used in volumetric analysis, but if fluorides are present no satisfactory end-point can be reached. If excess of pyrophosphate is present the ferric ion concentration is reduced to such a degree that the reverse change takes place, and ferrous salts can be titrated with iodine in such solutions.

Permanganates.—Oxidation of ferrous solutions with potassium permanganate is a well-known operation of volumetric analysis:

$$5Fe^{..}+MnO_4'+8H^{.}=5Fe^{...}+Mn^{..}+4H_2O,$$
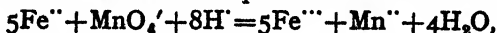
but if hydrochloric acid is present the end-point is sometimes unsatisfactory. It can be much improved by the addition of phosphoric acid, which reduces the ferric ion concentration almost to zero.

Dichromates.—The oxidation of ferrous salts by dichromate is also much used in volumetric analysis:

$$6Fe^{..}+Cr_2O_7''+14H^{.}=6Fe^{...}+2Cr^{...}+7H_2O,$$
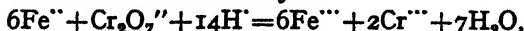
especially since it has been found that diphenylamine can be used as a very sensitive internal indicator. This titration is also facilitated by the addition of phosphoric acid.

Copper Salts.—The standard electrode potential of copper with respect to cupric ions is $+0.34$ volt, so that in neutral solution ferric salts are quantitatively reduced by copper to ferrous salts:

$$2Fe^{...}+Cu \downarrow \rightarrow 2Fe^{..}+Cu^{..}.$$
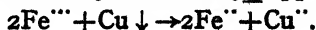
However, the reverse change takes place in alkaline solution:

$$2Fe(OH)_3 \downarrow +Cu^{..}+2OH' \rightarrow 2Fe(OH)_2 \downarrow +Cu \downarrow.$$

If excess of fluoride is present, ferrous salts will reduce cupric salts to copper even in acid solution, while in neutral solution a cuprous salt is produced:

$$Fe^{..}+Cu^{..} \rightarrow Fe^{...}+Cu^{.}.$$
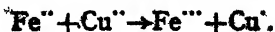
Silver Salts.—The standard electrode potential of silver is $+0.80$ volt, close to the ferric-ferrous oxidation potential, so, as might be expected, the precipitation of silver from solutions of silver salts by ferrous solutions reaches an equilibrium:

$$Fe\cdot\cdot+Ag\cdot\rightleftharpoons Fe\cdot\cdot\cdot+Ag\downarrow.$$

At room temperature the action is a slow one, and may take an hour or two to reach practical equilibrium.

Organic Anions.—The oxidation of organic anions by ferric solutions is usually much influenced by light. With oxalates, the reaction is:

$$2Fe\cdot\cdot\cdot+C_2O_4''=2Fe\cdot\cdot+2CO_2\uparrow.$$
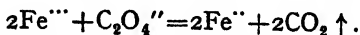
A mixed solution of a ferric salt and oxalic acid is perfectly stable at room temperature in the dark, though it decomposes on boiling, but if exposed to light it immediately begins to give off carbon dioxide even in the cold; the reaction is over in a few minutes. A similar reaction is made use of in the preparation of ' blue prints.' The paper is soaked in a solution of the ferric salt of an organic acid and dried in the dark. It is then covered with a drawing made on transparent paper and exposed to the light. Washing in the dark with a solution of a ferricyanide then reveals the drawing in white lines on a background of prussian blue.

Sulphides.—See ferric sulphide (p. 792).

Carbonates.

Ferrous carbonate, $FeCO_3$, is obtained as a white precipitate from ferrous solutions and carbonate solutions in the absence of air. If a current of carbon dioxide is passed through the liquid, the precipitate dissolves to form a bicarbonate solution.

Ferric carbonate is unknown, but a basic carbonate can be precipitated from ferric solutions by carbonates. It is hydrolysed by boiling water into ferric hydroxide and carbon dioxide.

Halides.

Since the ferric-ferrous oxidation potential is 0.77 volt, and the standard electrode potentials of the halogens are: F $+2.85$, Cl $+1.358$, Br $+1.065$, I $+0.535$ volt, it is clear that ferric iodide cannot exist in solution. Indeed it is unknown either in solution or in the solid state. Ferric bromide is stable in cold water but is decomposed on boiling.

The ferrous halides are prepared by the action of hydrogen halides on the metal in the absence of air, either in solution or in the dry state. The bromide or iodide can be made from the halogen and the hot metal. Alternatively, the ferrous halides may be prepared by reducing the ferric halides, carefully, with hydrogen; on too

strong heating the metal is obtained. The ferric halides are made by the action of halogens on iron or on the ferrous halides, or by the action of hydrogen halides on ferric hydroxide.

The ferrous halides are true salts highly ionized in solution; the fluoride and chloride have high melting-points. The ferric halides are largely covalent. The fluoride, as is the case with other elements, differs somewhat in character from the chloride and bromide, but these two compounds either have low melting-points or decompose on heating, are partially hydrolysed by water, and dissolve in organic solvents: they resemble the halides of aluminium or chromium.

Ferrous fluoride, FeF_2, is a colourless solid which volatilizes at about 1100°: it is soluble in water.

Ferric fluoride, FeF_3, resembles aluminium fluoride. It is fairly volatile at about 1000°, and the anhydrous salt is scarcely soluble in water, but hydrates have been prepared that will dissolve. The electrical conductivity of these solutions indicates that both dissociation and hydrolysis are very slight. Ferric fluoride is converted to ferric hydroxide by moist air or steam. With fluoride ions the complexes FeF_6''' and $FeF_5.H_2O''$ are formed, and many *fluoferrates* containing these anions have been prepared in the solid state. The ferric ion concentration of fluoferrate solutions is insufficient to give a red colour with thiocyanates. The fluoferrates of sodium and potassium are only slightly soluble in water, and *sodium fluoferrate*, Na_3FeF_6, is obtained as a white precipitate when a ferric solution is mixed with a solution of sodium fluoride.

Ferrous chloride, $FeCl_2$, whether in the solid state or in solution, is perfectly colourless if quite free from the ferric salt, but in the air the solid rapidly grows yellow and the solution green. It melts at a red heat and can be distilled at higher temperatures, the vapour density pointing to some association into double molecules; but at high temperatures these are completely dissociated into single molecules. Cryoscopic measurements in such organic liquids as will dissolve the salt also indicate the simple formula. The anhydrous salt is very soluble in water, and readily forms hydrates (of which the best known is the tetrahydrate, $FeCl_2.4H_2O$), and addition-compounds with ammonia. It is also soluble in alcohol.

Ferric chloride, $FeCl_3$, is usually made from chlorine and hot iron. Like aluminium chloride, it is decomposed by moist air, so suitable precautions must be taken in making it. The crystals of the anhydrous compound, which are dark red (almost black) with a green reflection, sublime at 285°, and the liquid can exist only under more than atmospheric pressure. The vapour consists almost entirely of double molecules at low temperatures, but on heating, dissociation into single molecules takes place, and on further heating, ferric chloride dissociates into ferrous chloride and chlorine:

this dissociation is appreciable at 500°. In organic solvents ferric chloride has the simple formula.

The anhydrous salt is deliquescent and forms several hydrates whose solubility relations have already been discussed (p. 131), as well as various addition-compounds with ammonia. The hydrolysis of the solutions has been the object of much research. If dilute and freshly prepared, they are almost colourless, but they slowly become deep yellow or brown, while the colloidal solutions of ferric hydroxide obtainable with boiling water may be blood-red. The electrical conductivity also increases with time. Hydrolysis alone is scarcely sufficient to account for these changes, as hydrolyses of this ionic type are nearly always rapid and indeed instantaneous processes. It is probable that the properties of the solution are also influenced by slow changes in the constitution of the colloid. The aqueous solutions certainly contain very few simple ferric ions, but all combinations of $Fe^{\cdot\cdot\cdot}$ with Cl' from $FeCl^{\cdot\cdot}$ to $FeCl_3$ are probably present. The clear yellow colour of solutions in hydrochloric acid is due to the repression of hydrolysis and the formation of complex halide ions, such as $FeCl_4'$ and $FeCl_6'''$.

Ferric chloride is very soluble in many organic solvents. A definite distribution-ratio can be obtained for it between ether and concentrated hydrochloric acid, and with acid of carefully chosen concentration—about 6·6 molar—the ratio is so greatly in favour of the ether layer that ethereal extraction has been used as a method of removing iron compounds from mixtures with those of closely related elements such as cobalt. The existence of such a ratio is strong evidence for the imperfect dissociation of ferric chloride in aqueous solution, and may be contrasted with the behaviour of hydrogen chloride (p. 184).

With chlorides ferric chloride forms salts called *chloroferrates*, but as usual they are much less stable than the complex fluorides and the covalency of the iron may be less. The principal anions are $FeCl_4'$ and $[FeCl_5.H_2O]''$; of the anion $FeCl_6'''$, corresponding with FeF_6''', only few salts have hitherto been prepared.

Ferrous bromide, $FeBr_2$, is a yellow crystalline substance resembling the chloride. It may be prepared anhydrous by heating iron in bromine vapour to a temperature sufficient to decompose any ferric bromide and cooling in carbon dioxide.

Ferric bromide, $FeBr_3$, may be prepared by gently heating iron in bromine vapour. On heating alone, or on boiling the aqueous solution, it decomposes into ferrous bromide and bromine.

Ferrous iodide, FeI_2, is made by union of the elements. In the presence of water, the reaction takes place in the cold with the development of heat. The anhydrous salt is a grey solid melting at 177°; it is deliquescent and soluble in water. Atmospheric

2 C

oxidation of the solutions leads to the separation of iodine, as ferric iodide cannot exist in solution.

SULPHIDES.

Ferrous sulphide, FeS, is obtained by precipitating ferrous solutions with sulphides, such as ammonium sulphide, in alkaline solution. In neutral solution precipitation is incomplete, and in acid solution no precipitation takes place. The hydrated sulphide obtained in this way is a black substance. The anhydrous substance is easily obtained by union of the elements at a red heat, or by heating iron in a current of hydrogen sulphide. It is a bluish-black substance with a high melting-point, but when heated in the air it readily forms ferrous sulphate, which decomposes on stronger heating.

The decomposition of ferrous sulphide by acids is often used, in Kipp's apparatus or otherwise, for the preparation of hydrogen sulphide, but if natural ferrous sulphide is used the gas obtained is far from pure.

Ferric sulphide, Fe_2S_3.—Ferric ions can oxidize sulphide ions to sulphur:

$$2Fe^{\cdots}+S''\rightleftharpoons 2Fe^{\cdot\cdot}+S\downarrow,$$
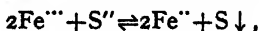
and ferric sulphide can be precipitated only from alkaline solutions, in which its solubility is too small for this change to take place. Thus the addition of a small quantity of ammonium sulphide solution to a solution of a ferric salt causes the precipitation of a mixture of ferrous sulphide and sulphur:

$$2Fe^{\cdots}+3S''\rightarrow 2FeS\downarrow+S\downarrow,$$
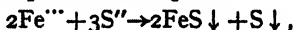
but if a little ferric salt is added to excess of ammonium sulphide solution, ferric sulphide is precipitated:

$$2Fe^{\cdots}+3S''\rightarrow Fe_2S_3\downarrow.$$
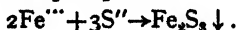
It is best prepared by passing hydrogen sulphide through a suspension of ferric hydroxide in water, since such a solution cannot become acid. Ferric sulphide is a black substance decomposed by acids into a ferrous salt, sulphur, and hydrogen sulphide:

$$Fe_2S_3+4H^{\cdot}=2Fe^{\cdot\cdot}+S\downarrow+2H_2S\uparrow.$$
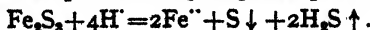
The fact that ferric sulphide, but not aluminium sulphide, can under certain circumstances be precipitated from aqueous solution may perhaps be attributed to the lower solubility of the former.

Metallic ores, such as *chalcopyrite*, $CuFeS_2$, or *mispickel*, FeAsS, containing iron and sulphur in conjunction with other metals, are very widespread in nature.

Iron disulphide, FeS_2, occurs in nature as the important and abundant mineral *iron pyrites*. It can be obtained artificially by boiling ferrous sulphide with sulphur, and by many other processes.

It is a yellow substance, insoluble in water, which on strong heating in the absence of air decomposes into ferrous sulphide and sulphur, and is to be regarded as a polysulphide. The roasting of iron pyrites was for many years the commonest commercial method for the preparation of sulphur dioxide for sulphuric acid manufacture. Atmospheric oxidation of pyrites in the presence of moisture leads to the formation of ferrous sulphate and sulphuric acid:

$$2FeS_2 + 2H_2O + 7O_2 = 2Fe^{..} + 4H^. + 4SO_4'',$$
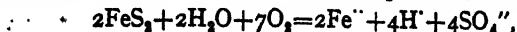
and this is the origin of the ferrous sulphate often to be found in the drainage water of coal mines.

SULPHATES.

Ferrous sulphate, $FeSO_4$, is prepared on the large scale from pyrites. The solution obtained by atmospheric oxidation is treated with old iron, which not only forms ferrous sulphate with the sulphuric acid, but also precipitates in the metallic form any copper which may be present as cupric salt. The product obtained by crystallizing the solution is not pure, and pure ferrous sulphate is prepared from pure iron and dilute sulphuric acid. Crystallization at room temperature yields crystals of the heptahydrate $FeSO_4.7H_2O$, formerly known as ' green vitriol.' The anhydrous salt can be prepared by carefully heating the heptahydrate in the absence of air, but some basic salt may be formed at the same time. Anhydrous ferrous sulphate is a colourless substance which when strongly heated decomposes into ferric oxide, sulphur dioxide, and sulphur trioxide:

$$2FeSO_4 = Fe_2O_3 + SO_2 \uparrow + SO_3 \uparrow.$$
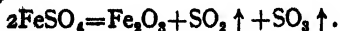
Fuming sulphuric acid was for many years prepared by the distillation of green vitriol, especially at Nordhausen (Germany), whence the name ' Nordhausen acid.'

Ferrous sulphate is soluble in water. The solutions are oxidized by the air, but the rate of oxidation can be much reduced by the addition of dilute sulphuric acid, which prevents the formation of colloidal ferric hydroxide. Even the slight acidity of an ammonium salt solution is sufficient for the purpose, and consequently the double salt ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$, is nearly always preferred to ferrous sulphate for the analytical operations in which ferrous sulphate is often used as a reducing agent.

Ferrous sulphate solutions have the property of absorbing nitric oxide. The solutions are brown, and since at saturation one molecule of nitric oxide is present per molecule of ferrous sulphate, it is reasonable to suppose that a compound, $FeSO_4.NO$, is present, or more probably an ion, $(Fe.NO)^{..}$, since other ferrous solutions have the same property. This view has been confirmed by the

isolation of such a compound by adding concentrated sulphuric acid to the solution, when it appears in red crystals, which easily decompose. The production of this brown solution is the basis of the brown ring test for nitrates or nitric acid. The suspected solution is mixed with ferrous sulphate solution in a tube, and concentrated sulphuric acid is carefully poured down the side so as to form a separate lower layer. Heat is developed at the surface of separation, and in the hot strongly acid solution the ferrous sulphate reduces the nitric acid to nitric oxide, which dissolves to form a brown ring.

Ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$, is a pale green salt obtained by cooling mixed saturated solutions of ferrous and ammonium sulphates. Many other double sulphates containing ferrous iron are known.

Ferric sulphate, $Fe_2(SO_4)_3$, is prepared by carefully heating ferrous sulphate in the air, or more easily by boiling it with concentrated sulphuric acid:

$$2Fe^{..}+4H^{.}+SO_4{''}=2Fe^{...}+SO_2\uparrow+2H_2O.$$
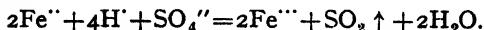
The anhydrous salt obtained in this way is a colourless solid which when strongly heated yields ferric oxide and sulphur trioxide, which is itself partly decomposed into sulphur dioxide and oxygen. It is soluble in water, and from the solution a number of hydrates can be obtained, such as the violet enneahydrate $Fe_2(SO_4)_3.9H_2O$, but evaporation at high temperatures leads to the separation of acid and basic salts. Ferric sulphate readily forms alums in which the aluminium is replaced by ferric iron, e.g. *ferric ammonium sulphate*, 'ferric alum,' $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$. Solutions of this substance are strongly hydrolysed, and if highly diluted deposit precipitates.

NITRATES.

Ferrous nitrate, $Fe(NO_3)_2.6H_2O$.—Since nitrates oxidize ferrous salts on boiling, even in neutral solution, the preparation of ferrous nitrate requires considerable care, and the anhydrous salt has never been obtained. It is present in the solution prepared by dissolving iron in very dilute nitric acid, and it has also been prepared in solution by the double decomposition of lead nitrate and ferrous sulphate in dilute alcohol. By filtering this solution and evaporating it in the cold it is possible to obtain ferrous nitrate hexahydrate. It is very soluble in water, but is decomposed above 60° with the precipitation of ferric hydroxide.

Ferric nitrate, $Fe(NO_3)_3$, can be obtained in hydrated form by dissolving iron in nitric acid sufficiently concentrated to avoid the formation of ferrous nitrate, but not so concentrated as to render

the metal passive. A dark red solution is obtained, from which concentrated nitric acid precipitates the hydrated salt. The anhydrous compound is unknown. If perfectly pure, ferric nitrate is colourless, but as usually obtained it is pale violet.

PHOSPHATES.

Ferrous orthophosphate, $Fe_3(PO_4)_2.8H_2O$, is a colourless substance nearly insoluble in water and precipitated from ferrous solutions by phosphates under carefully controlled conditions of acidity.

Ferric orthophosphate, $FePO_4.2H_2O$, is a pale yellow substance obtained from ferric solutions in a similar way, or by dissolving iron in concentrated phosphoric acid and oxidizing the resulting solution in the air. It is practically insoluble in water but is hydrolysed by boiling water.

CARBONYLS.—Iron forms three compounds with carbon monoxide.

Iron pentacarbonyl, $Fe(CO)_5$, is prepared by the action of carbon monoxide on finely-divided iron. It is a pale yellow liquid, freezing at $-20°$ and boiling at $103°$; on stronger heating it is decomposed into iron and carbon monoxide. The vapour density and the freezing-point of benzene solutions both point to the simplest molecular weight. The action of halogens X_2 produces compounds $Fe(CO)_4X_2$, which are covalent like the parent carbonyl, but are completely decomposed by water into ferrous salt and carbon monoxide. In sunlight the pentacarbonyl decomposes:

$$2Fe(CO)_5 = Fe_2(CO)_9 + CO \uparrow .$$
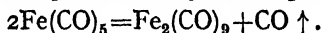
Iron enneacarbonyl, $Fe_2(CO)_9$, formed in this reaction is an orange-coloured crystalline solid, which, unlike the pentacarbonyl, is insoluble in benzene or ether, and can be isolated from it with the help of these solvents. It decomposes on warming to about $100°$ or over:

$$2Fe_2(CO)_9 = 3Fe(CO)_5 \uparrow + 3CO \uparrow + Fe,$$

but at lower temperatures, and in the presence of suitable solvents, such as toluene, green solutions of *iron tetracarbonyl*, $Fe(CO)_4$, are obtained. This is a green crystalline substance which at $150°$ decomposes into iron and carbon monoxide. The molecular weight corresponds with the formula $[Fe(CO)_4]_3$.

COMPLEX IRON CYANIDES.

Iron forms complex anions of great stability with six cyanide groups per iron atom. The ferrous derivatives are called *ferrocyanides* and contain the anion $Fe(CN)_6''''$, the ferric derivatives, or *ferricyanides*, contain the anion $Fe(CN)_6'''$. The ferrocyanides must exceed the ferricyanides in stability, since the ferricyanide-ferrocyanide oxidation potential is slightly greater than the ferric-ferrous oxidation

potential.   Ferricyanides will oxidize ferrous salts to ferric salts, so that ferric ferrocyanide is produced either by adding a ferric salt to a ferrocyanide or a ferrous salt to a ferricyanide:

$$Fe(CN)_6''' + Fe'' \rightarrow Fe(CN)_6'''' + Fe'''.$$
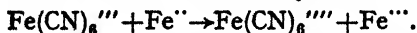
Moreover, ferricyanides will partially oxidize hydrochloric acid to chlorine:

$$2Fe(CN)_6''' + 2Cl' \rightleftharpoons 2Fe(CN)_6'''' + Cl_2 \uparrow,$$
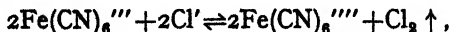
whereas ferric ions will not liberate chlorine from chloride solutions.

Like many other oxidation-reduction systems, that of ferricyanide-ferrocyanide is markedly influenced by the hydrogen ion concentration of the solution containing the system: indeed a change in acidity to alkalinity reverses the character of the system from reducing to oxidizing powers.   In alkaline solution the oxidizing action of ferricyanide is shown in the equation:

$$2Fe(CN)_6''' + 2OH' \rightarrow 2Fe(CN)_6'''' + H_2O + O.$$
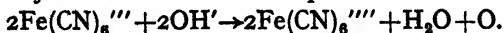
Alkaline solutions of ferricyanides will liberate oxygen on boiling, whereas in acid solution the change is reversed, and acid ferrocyanide solutions are oxidized by the air.

Ferrocyanides.—Many ferrocyanides are insoluble in water, but those of the alkali- or alkaline-earth metals are not.   The soluble ferrocyanides can be prepared in solution by adding ferrous salts to cyanides:

$$Fe'' + 6CN' \rightarrow Fe(CN)_6'''',$$
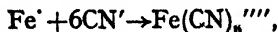
while the insoluble ferrocyanides are usually prepared by precipitation from solutions of potassium ferrocyanide.   In many insoluble cyanides, e.g. silver cyanide, and in prussian blue both atoms of cyanide ion act as donors: in ferro- and ferricyanides carbon is the donor atom.

Potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$, ' yellow prussiate of potash,' is obtained in the laboratory as described or by dissolving iron in cyanide solutions.   It is obtained on the large scale as a by-product in the purification of coal-gas.   The crude gas contains hydrogen cyanide and some ammonia, from which it is freed, in one process, by passage through a solution of ferrous sulphate. Potassium ferrocyanide can be obtained from the resulting solution by boiling it with lime and adding potassium carbonate, which precipitates the calcium as carbonate.   It can be purified by precipitating the saturated aqueous solution with alcohol.

It is a yellow crystalline substance soluble in water, and can be dehydrated by heating; the anhydrous salt is colourless.   Unlike potassium cyanide, it is non-poisonous.   If strongly heated in the absence of air it yields potassium cyanide, cyanogen, and iron:

$$K_4Fe(CN)_6 = 4KCN + C_2N_2 \uparrow + Fe.$$
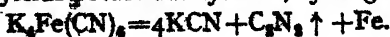
With dilute acids hydrogen cyanide is obtained:

$$Fe(CN)_6'''' + 6H^. = 6HCN \uparrow + Fe^{..},$$
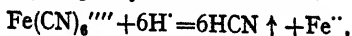
but with concentrated sulphuric acid, to which a little water may be added with advantage, pure carbon monoxide is liberated on heating:

$$Fe(CN)_6'''' + 12H^. + 6H_2O = Fe^{..} + 6NH_4^. + 6CO \uparrow.$$
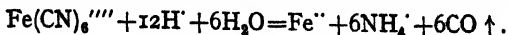
With *ferrous* solutions, potassium ferrocyanide produces a white precipitate of potassium ferrous ferrocyanide, $K_2Fe[Fe(CN)_6]$, easily oxidized by the air, and with *ferric* solutions a precipitate, or in very dilute solutions a blue colloidal solution, of 'prussian blue,' $KFe_2(CN)_6$.Aq. Turnbull's blue is produced from potassium ferricyanide solutions by addition of solutions of ferrous salts. Ferrocyanides are easily oxidized to ferricyanides by chlorine, permanganates, and other oxidizing agents, and some of these actions are made use of in volumetric analysis.

Ferrocyanic acid, $H_4Fe(CN)_6$, is obtained as a colourless precipitate by the action of concentrated hydrochloric acid on a saturated solution of potassium ferrocyanide. It is soluble in water, and the solution is strongly acid. When boiled it decomposes into hydrogen cyanide and ferrous cyanide, and the same change takes place when the solid is dried and heated in the absence of air. Solutions of ferrocyanic acid, or the solid substance, are easily oxidized by the air.

Prussian blue and *Turnbull's blue*, which are insoluble, and the so-called 'soluble' blue all have essentially the same composition, $K[Fe_2(CN)_6]$, but contain differing amounts of hydrate water. The anion $[Fe_2(CN)_6]'$ owes its existence to the fact that cyanide ion can develop two, collinear co-ordinate links ($\leftarrow CN \rightarrow$). Each cyanide is common to two structural units, in each of which an iron atom is surrounded octahedrally by six cyanide groups, but in one set the linkages are of the type $Fe \leftarrow CN$ and in the other $Fe \leftarrow NC$. Since every CN provides two links, and every atom of iron receives six, the composition of the anion is explained. In the unit-cell an iron atom is found at each of the corners of a cube, and a CN group along each edge. As this structure is proliferated to give the (macromolecular) structure of the actual solid, potassium ions necessary for electro-neutrality are placed in alternate cubes. Iron atoms are formally present in equal numbers in the ferrous and ferric states, and the characteristic colour is caused by the interchangeability of these states.

Ferricyanides.—*Potassium ferricyanide*, $K_3Fe(CN)_6$, 'red prussiate of potash,' is prepared by oxidizing potassium ferrocyanide in solution, usually with chlorine:

$$2Fe(CN)_6'''' + Cl_2 \rightarrow 2Fe(CN)_6''' + 2Cl'.$$
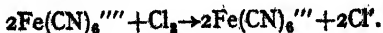
In boiling solution the reaction is reversible.   The product is freed from potassium chloride by recrystallization, and is a red solid which dissolves in water to form a yellow solution.   Ferricyanide solutions are· slightly hydrolysed and may precipitate ferric hydroxide, particularly if they are exposed to the light.   They are mild oxidizing agents which will oxidize iodides, bromides, and to some extent chlorides to the element and hydrogen sulphide to sulphur. With hydrogen peroxide in *alkaline* solution (p. 341) mutual reduction takes place according to the equation:

$$2Fe(CN)_6''' + H_2O_2 = 2Fe(CN)_6'''' + 2H\cdot + O_2 \uparrow .$$
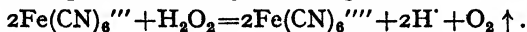
Ferricyanic acid, $H_3Fe(CN)_6$, is prepared in solution from hydrochloric acid and silver ferricyanide, or as a brown solid by the evaporation of this solution at room temperature.

Ferric thiocyanate, $Fe(CNS)_3.3H_2O$.—The addition of soluble thiocyanates to ferric solutions, which if dilute are usually acidified to avoid hydrolysis, produces a red colour so intense that it is the most sensitive known test for ferric iron.   Ferric thiocyanate is very soluble in ether, and can be extracted from its aqueous solutions with this solvent.   The ethereal solution is deep red, and shaking with ether intensifies the delicacy of the thiocyanate test for iron. By evaporating the solvent deep red crystals of composition $Fe(CNS)_3.3H_2O$ have been obtained, but their constitution, which might be represented as $Fe[Fe(CNS)_6]$, has not yet been ascertained.

COBALT AND NICKEL

Co=58·94; *atomic number,* 27   Ni=58·71; *atomic number,* 28

History.—(*a*) COBALT.—Though the name *kibaltu,* applied to a certain mineral, has been found in Assyrian glass-making recipes of the seventh century B.C., it is as yet uncertain whether the word is etymologically affiliated to *cobalt.*   It is true that cobalt ores were used by the Assyrians and Egyptians in preparing blue glass and faience, but the name ' cobalt ' is usually supposed to be derived from the German *Kobold,* an evil sprite.   These sprites or gnomes lived in the copper mines in the Harz Mountains, and took pleasure in exposing ores that looked like copper ores but on roasting gave an unpleasant smell and no copper.   These false ores were called kobold ores or cobalt ores.   BRANDT (1735) showed that cobalt ore contained a new metal, the properties of which were afterwards more fully investigated by BERGMANN (1780).

(*b*). NICKEL.—A further ore, deceptively like copper ore, was described by the unfortunate German miners as *Kupfernickel,* i.e. ' false copper.'   From this ore KRONSTEDT (1751) obtained metallic

nickel; it was, however, again BERGMANN (1774) who first accurately described the metal and certain of its compounds.

Occurrence and Extraction.—*Cobalt* is much less abundant than iron. The principal ores are in Cobalt District, Ontario, Canada, where arsenides and mixed arsenides and sulphides of the metal are mined. *Smaltite*, $CoAs_2$, is also found in Germany, and *cobaltite*, CoAsS, in Sweden. Cobalt is always associated with nickel in its ores, and often with silver.

The process of extraction adopted in Canada is briefly as follows. The ore is crushed, finely ground, and smelted in a blast furnace with the addition of sand and limestone for flux. At the end of this operation some crude silver has separated, and this is removed and refined. The product is mixed with common salt and roasted, and is then cooled and extracted with water, the cobalt, copper, and some nickel passing into solution as chlorides. The copper is precipitated with iron scrap, and the cobalt and nickel separated as hydroxides by the addition of caustic soda. The precipitate is washed, dissolved in hydrochloric acid, and treated with calcium carbonate to remove any iron or silica. The filtrate is then treated with bleaching powder, which precipitates nearly all the cobalt as the hydrated sesquioxide, leaving nearly all the nickel in solution. From this oxide the metal can be prepared by various methods; either by heating with charcoal, or by GOLDSCHMIDT'S process, or by reduction with hydrogen, or electrolytically.

In the laboratory the preparation of *pure cobalt* or cobalt compounds presents some difficulty. Reliable methods are available for the removal of nickel—e.g. the dimethylglyoxime precipitation —but the last traces of iron are hard to get rid of. Commercial samples of cobalt salts all contain iron, sometimes in quite large proportions. The process generally recommended is to prepare chloropentammino cobalt chloride, $[CoCl.5NH_3]Cl_2$, to purify it by precipitating the ammoniacal solution several times with pure hydrochloric acid, and then to use it as a source of pure cobalt compounds.

Nickel is more abundant than cobalt, but much less so than iron. The most important sources of nickel are in Ontario, where it occurs in sulphides and arsenides associated with copper pyrites: and the deposits of *garnierite*, a mixed silicate of magnesium and nickel mined in New Caledonia, are also of commercial importance.

The extraction of nickel from its ores is a somewhat complicated process which varies according to the nature of the ore. During the greater part of the nineteenth century no economical method of extraction had been discovered, and consequently nickel was little used. The discovery of the volatile compound nickel carbonyl, $Ni(CO)_4$, in 1890 suggested a method of separation which is now

*2 C

worked on a very large scale, and to which the modern industrial importance of the metal is due.

The Canadian ores are first roasted in the open, then mixed with slag from the converter and smelted in a blast furnace. The product is then transferred to a Bessemer converter similar to that used in steel manufacture, mixed with a flux, and oxidized in an air-blast. This process removes most of the iron as silicate, and leaves a mixture of nickel and copper sulphides which is sent to the refinery for further treatment. A large proportion of the world's production of nickel is made by the MOND carbonyl process originally installed at Swansea in South Wales.

At the refinery the sulphides are first roasted to oxides, and these are then treated with hot dilute sulphuric acid, which dissolves out nearly all the cupric oxide while leaving nearly all the nickel oxide. The product of this process is an important source of copper. The undissolved oxides are reduced to the metal by producer-gas, and the metal is then heated to about 60° in an atmosphere of carbon monoxide. The nickel carbonyl produced is passed into a chamber filled with moving nickel shot and kept at 200°. At this temperature it is decomposed into nickel and carbon monoxide: the nickel is deposited on the shot as metal of at least 99·8 per cent purity, and the gas is used again. After the crude metal obtained by reduction has twice been through the carbon monoxide process, the residues are worked up for the metals of the platinum group. Nickel can also be refined electrolytically, and in this way can easily be freed from iron.

In the laboratory *pure nickel* compounds can be obtained from hexammino nickel bromide, $[Ni.6NH_3]Br_2$.

Uses.—*Nickel* was put to commercial use many years before cobalt, and, chiefly on account of its lower cost, is still of much greater practical importance. Nickel and its alloys are hard and resist corrosion or oxidation, and nickel is used on a large scale for electroplating, or as an impervious electroplated foundation for chromium plating. This is usually carried out in hot ammoniacal solution, in which the nickel is present as a complex ion. The bright parts of motor cars and bicycles are often nickel-plated. Of the alloys of nickel, nickel steels absorb more than half the total production of the metal. Of the special alloys, *invar* contains about 35 per cent of nickel, with a little manganese and carbon, and the rest iron. It has an exceedingly small coefficient of expansion, takes a high polish, and is very resistant to corrosion; it is therefore much used in watches, clocks, and other apparatus of the kind. *Platinite* has a higher proportion of nickel, about 46 per cent, and a coefficient of expansion equal to that of soda-glass, so it is used as a substitute for platinum for sealing into glass. *Nichrome* contains 60 per cent of nickel, 14 per cent of chromium, and the rest

iron, and is used as resistance wire and for electrical heating; its advantages being its high specific resistance, high melting-point, and resistance to oxidation or chemical attack. Of the alloys with copper, that containing 25 per cent of nickel and 75 per cent of copper is used in coinage in the United States and in Europe, and that containing 40 per cent of nickel and 60 per cent of copper is called *constantan* and is used in thermo-couples. *Monel metal*, which contains 60 per cent of nickel and 35 per cent of copper, with some iron, is very resistant to corrosion and is used in chemical plant: it is prepared directly from ores of nickel and copper. Finally, *German silver*, used in plate and for ornaments, is an alloy of copper, nickel, and zinc which may contain copper 55 per cent, nickel 25 per cent, zinc 20 per cent.

Nickel crucibles are used in the laboratory for alkaline fusions, but are inferior to silver crucibles for this purpose: nickel spatulas are also popular. Nickel is also used in the EDISON accumulator.

Cobalt is principally used in the cobalt steels, suitable for high-speed cutting tools. The addition of cobalt to steel greatly increases the magnetic retentivity. Since cobalt is harder than nickel, cobalt-plating can be made thinner than nickel-plating without loss of protection, and the nickel of nichrome can also be advantageously replaced by cobalt. An alloy of cobalt and chromium is used as a constituent of 'stainless steel.' Cobalt oxide gives a fine blue colour to glass and porcelain, and small quantities are used for this purpose.

Properties.—Cobalt and nickel are silver-white magnetic metals of density about 8·8, but the cast metals are less dense. Cobalt is noticeably brighter than nickel. In the massive form they are both resistant to oxidation, but the finely-divided metals obtained by reducing the monoxide at a low temperature, e.g. 200°, in hydrogen are pyrophoric. Even in the massive form the metals can be superficially oxidized by strong heating in air or oxygen. They are hard, but malleable and ductile.

The standard electrode potentials of both cobalt and nickel are between —0·277 and —0·230 volt. This means that the metals are not attacked by water and only slowly by dilute acids, but they will decompose steam at a red heat. In concentrated nitric acid they display passivity.

Cobalt and nickel resemble iron in appearance, density, melting-point, and in the possession of magnetic properties, but have greatly superior resistance to corrosion and are also much less abundant. The bivalent compounds of the three elements show considerable resemblance to each other, as will appear from the account given in the following pages, and a further link is afforded by the carbonyls of all these elements.

Finely-divided nickel, usually prepared by reducing the monoxide at a low temperature with hydrogen, has long been used in the laboratory as a catalytic agent in the hydrogenation of gases: thus the oxides of carbon, when mixed with hydrogen and passed over hot catalytic nickel, are converted to methane and water. Among the earliest investigators in this field were SABATIER and SENDERENS. In more recent years the process has been applied on a manufacturing scale to the hardening of fats. Thus whale-oil, even when deodorized, is a liquid in itself of little value, but when mixed with nickel and exposed to hydrogen under pressure it takes up the gas and forms a fat, solid at ordinary temperatures, which can be used in the manufacture of soap—though its advantages for this purpose are chiefly confined to its low cost. The nickel is recovered, purified, and used again.

COMPOUNDS OF COBALT AND NICKEL.—The chemistry of these elements resembles that of iron, but, if their complex derivatives are excluded, is less complicated, since the tervalent state so important in the study of the iron compounds is inconspicuous with cobalt and almost absent with nickel, which is incapable of forming a tervalent cation. Consequently the stability of the bivalent state increases from iron to nickel, and the oxidation potential $Co^{...} \rightarrow Co^{..}$ is 1·82 volts, a very high value as compared with 0·77 volt for $Fe^{...} \rightarrow Fe^{..}$. In the numerous and often very stable cobaltic complexes, the metal is, however, tervalent.

The bivalent cations of cobalt and nickel, in the presence of excess of water, are red and green respectively.

OXIDES AND HYDROXIDES.—In addition to the oxides and hydroxides in which the elements are bivalent, both cobalt and nickel form higher oxides, though the identity and properties of some of them are uncertain. Cobalt forms compounds $Co_2O_3.H_2O$ and Co_3O_4, nickel probably only Ni_2O_3.

Cobaltous hydroxide, $Co(OH)_2$, is a blue precipitate obtained by the addition of caustic alkalis to cobaltous solutions. It turns pink on boiling, and a pink solid is directly obtained by adding cobaltous solutions to aqueous alkali. Without colour change each precipitate gives the hydroxide $Co(OH)_2$ on drying. The blue hydroxide is readily oxidized if exposed to the air, and then turns brown. It is not quite insoluble in water; the solubility is about 3 milligrams per litre at 20°. It will dissolve in concentrated ammonia (though less readily than nickelous hydroxide) to form a complex cation, and the ammoniacal solutions are easily oxidized by the air to form cobaltammines in which the metal is tervalent.

Cobaltous oxide, CoO, is obtained by heating the hydroxide or carbonate in an inert atmosphere, or by careful reduction of the sesquioxide in hydrogen at not too high a temperature. It is a

grey solid which on heating in the air forms tricobalt tetroxide, Co_3O_4, and is reduced to the metal by strong heating in hydrogen. Both oxide and hydroxide dissolve in acids.

Tricobalt tetroxide, Co_3O_4, is a black solid which, unlike the corresponding oxide of iron, is not magnetic. It is obtained by heating any other oxide of cobalt in the air, or by strongly heating cobaltous nitrate. It is an oxidizing agent which liberates chlorine from hydrochloric acid.

Cobalt sesquioxide, Co_2O_3, exists only as the monohydrate, a black substance obtained by heating cobaltous nitrate very gently. When heated in the air it yields tricobalt tetroxide.

Cobaltic compounds.—The hydrated sesquioxide is the only stable simple cobaltic compound. Cobaltic alum, $(NH_4)Co(SO_4)_2.12H_2O$, can be prepared as blue crystals by anodic oxidation of cobaltous sulphate, with subsequent addition at $0°$ of excess of ammonium sulphate. Since the oxidation potential $Co^{...} \rightarrow Co^{..}$ is $1·82$ volts, cobaltic solutions are very powerful oxidizing agents. They decompose on gentle warming, liberating either oxygen or an oxidation product of the anions present—e.g. chlorine from chloride. It is a remarkable testimony to the stabilizing effect of co-ordination that while cobalt*ous* complexes are rather unstable, those of ter-valent cobalt are perhaps more stable than any other group of complex substances: for example, cold concentrated sulphuric acid does not remove ammonia from hexammino-cobaltic chloride, $Co(NH_3)_6Cl_3$.

Nickelous hydroxide, $Ni(OH)_2$, is an apple-green precipitate obtained by adding caustic alkalis to nickel solutions. It is rather more soluble than cobaltous hydroxide in water (about 13 milli-grams per litre at $20°$) and differs from it in being freely soluble in ammonia, to form the blue nickel-ammonia complex ion, though it is precipitated from the solution on boiling. It is stable in the air.

Nickelous oxide, NiO, is prepared by heating the hydroxide or the carbonate, or by heating the metal in steam to a red heat. It is a green solid which grows yellow on heating, easily soluble in acids, and easily reduced by heating in hydrogen.

Nickel sesquioxide is not known with certainty. The black substance obtained by adding alkaline hypochlorites to nickelous solutions is believed to be a hydrate $Ni_2O_3.H_2O$, and a similar product can be obtained by heating nickelous nitrate very gently, or by bubbling chlorine through a suspension of nickel hydroxide. It is an oxidizing agent which with acids liberates oxygen or an oxidation-product of the acid. When this hydrate is carefully heated in vacuo at about $140°$ it steadily loses both oxygen and water until the composition reaches that of NiO. It has been

suggested that an oxide of composition NiO_2 may be present in the oxidized precipitate but no confirmed evidence for this has been produced.

CARBONATES.—The addition of carbonates to cobaltous or nickelous solutions precipitates basic carbonates, but hydrated normal carbonates are obtained if a solution of sodium hydrogen carbonate is used as the precipitant. Cobaltous carbonate is pink, nickelous carbonate green.

HALIDES.—The cobaltous and nickelous halides may be prepared by the usual methods, though the attack of the halogens, other than fluorine, on nickel and cobalt is vigorous only if the metal is f divided and heated. The compounds are salt-like and have or fairly high melting-points. The hydrates can be prepared by evaporation of the solutions in the air, but on further heating these yield basic salts unless the air is replaced by the hydrogen halide: this applies even to the fluorides. The cobaltous halides show greater evidence of covalency than the nickelous halides; cobaltous chloride, for example, is soluble in ether, but nickelous chloride is not, and cobaltous chloride also appears to be the more volatile, and in its solutions to be the more inclined to the formation of complex ions and undissociated molecules. The chlorides of iron, nickel, and cobalt are all soluble in alcohol.

All the halides are soluble in water, though the anhydrous fluorides are only slightly soluble. They all form hydrates.

Cobaltous fluoride, CoF_2, is a red substance which can be prepared anhydrous by heating cobaltous ammonium fluoride, $CoF_2.2NH_4F$, in the absence of air. This double salt is prepared by fusing anhydrous cobaltous chloride with excess of ammonium fluoride. Cobaltous fluoride melts at 1200°–1300° and can be boiled at about 1400°. The dihydrate $CoF_2.2H_2O$, soluble in water and prepared by the usual methods, is decomposed by boiling water to form a basic salt.

Cobaltous chloride, $CoCl_2$, is prepared anhydrous by heating the hexahydrate in a current of hydrogen chloride. It can be freed from less volatile impurities, but not from the chlorides of iron or nickel, by subliming it in a strong current of hydrogen chloride or chlorine (the highest temperature of a gas-burner is required). The product avidly absorbs water, by which it is hydrolysed at temperatures above 100° or so. At room temperature the stable form is the red hexahydrate $CoCl_2.6H_2O$, which when gently heated yields first the pink $CoCl_2.2H_2O$, then the violet $CoCl_2.H_2O$, and at about 120°, the bright blue anhydrous salt, which will, however, be contaminated with oxide unless the final heating has been carried out in hydrogen chloride.

Anhydrous cobaltous chloride dissolves in alcohol, ether, and

some other organic solvents to form blue solutions. Cryoscopic measurements on these indicate the existence of double molecules at low temperatures, dissociated into single molecules on heating. The colour of the aqueous solutions has received much attention. These may be either red, blue, or any intermediate shade of purple, the blue colour being favoured by high concentration, high temperature, and the presence of free hydrochloric acid. Attempts to account for these changes fall into two groups: according to one view the red cobalt ion is more hydrated than the blue one—the formulae $Co.6H_2O^{..}$ (red) and $Co.4H_2O^{..}$ (blue) have been suggested —and according to the other the hydrated cobalt ion is red, and the blue colour is due to either undissociated molecules, or, more probably, to complex ions which may be $CoCl_4''$. The observed facts are too complex to be accounted for by either of these theories alone: they are probably both correct. The colour-changes have been used in sympathetic inks—dilute solutions of cobalt chloride, pink and invisible in the cold, but blue on heating—and in toys containing strips of paper pink in wet weather but blue in dry weather.

Cobaltous bromide, $CoBr_2$.—Numerous hydrates of this salt have been prepared, among them the reddish-purple $CoBr_2.6H_2O$ and the bluish-purple $CoBr_2.2H_2O$. The anhydrous salt, obtained at 130°, is bright green. The molecular weight of anhydrous cobaltous bromide in organic solvents corresponds with the simple formula $CoBr_2$.

Cobaltous iodide, CoI_2, is a black substance obtained by union of the elements, or in solution by the action of water and iodine on cobalt powder. The hexahydrate $CoI_2.6H_2O$ is dark red and so are the cold dilute solutions, but the hot solutions are green.

Cobaltic halides. — The oxidation - potential of the change $Co^{...} \rightarrow Co^{..}$, 1·82 volts, exceeds the standard electrode potentials of all the halogens except fluorine, so only the fluoride can be prepared.

Cobaltic fluoride, CoF_3, is obtained by union of the elements, or by electrolytic oxidation of solutions of cobaltous fluoride in concentrated aqueous hydrogen fluoride, as a green powder deposited at the anode.. Water decomposes it to form cobaltic hydroxide, which, like ferric hydroxide, appears to be a weak base, but it is soluble in concentrated sulphuric acid to form a brown liquid which decomposes on warming. On heating, it gives cobaltous fluoride and fluorine.

Nickelous fluoride, NiF_2, is prepared by the method used for cobaltous fluoride: it is a yellow substance with a high melting-point. Green hydrates soluble in water have been prepared.

Nickelous chloride, $NiCl_2$, is yellow when anhydrous, but the

well-known hexahydrate, $NiCl_2.6H_2O$, is green. The anhydrous salt is converted to oxide, evolving chlorine, if heated in the air, but in the absence of air it can be sublimed at a high temperature.

Nickelous bromide, $NiBr_2$, is yellow when anhydrous. The addition of ammonia to a concentrated aqueous solution precipitates violet crystals of $Ni(NH_3)_6.Br_2$. Since the corresponding compound of cobalt is soluble in water, this is a good method of preparing pure nickel compounds free from iron and cobalt.

Nickelous iodide, NiI_2, is black when anhydrous, but the hexahydrate, $NiI_2.6H_2O$, obtained by evaporation of the aqueous solutions, is green.

SULPHIDES.—Hydrogen sulphide has no action on slightly acid solutions of cobalt or nickel salts, but ammonium sulphide produces black precipitates of the hydrated *monosulphides* CoS and NiS. It is remarkable that these precipitates will not dissolve in dilute acids, though they cannot be precipitated from acid solution. The explanation of this phenomenon is believed to lie in the transformation of the sulphide, as soon as it is precipitated, into a more stable and less soluble form. In confirmation of this view, three different nickel monosulphides have been prepared, one soluble in dilute acids, the other two not soluble. Neither cobalt monosulphide nor nickel monosulphide is so easily oxidized by the air to the sulphate as is ferrous sulphide. Several higher sulphides of cobalt and nickel have been described.

SULPHATES.—The anhydrous sulphates of cobalt and nickel, $CoSO_4$ and $NiSO_4$, unlike the halides, can be prepared by heating the hydrates in the air: this is because sulphuric acid, being less volatile than the hydrogen halides, is more effective in preventing hydrolysis. They can both be prepared in solution without difficulty by the usual methods.

Cobaltous sulphate, $CoSO_4$, when anhydrous is a red substance stable up to 700° and only slowly dissolved by water. Cobalt is sometimes weighed in this form, but all the water is expelled from the hydrates of cobaltous sulphate only at 250° or over. The hydrates $CoSO_4.6H_2O$ and $CoSO_4.7H_2O$, likewise red, are very soluble in water, and several other hydrates have been prepared.

Nickelous sulphate, $NiSO_4$, is yellow when anhydrous, while the hydrates are green or blue: it resembles cobaltous sulphate. *Nickel ammonium sulphate*, $NiSO_4.(NH_4)_2SO_4.6H_2O$, prepared from solutions of nickel sulphate and ammonium sulphate in sulphuric acid, is much used in nickel-plating. It is less soluble in water than is nickel sulphate.

Cobaltic sulphate, $Co_2(SO_4)_3$, is prepared by electrolysis of a solution of cobaltous sulphate in sulphuric acid, when it is precipitated in pale blue crystals at the platinum anode (high oxygen

over-voltage). The action of ozone on such a solution yields a similar product. It dissolves in water, but the dissolved salt slowly oxidizes the water to oxygen; the unstable solution is blue. An ammonium alum of tervalent cobalt has also been prepared by electrolysis.

NITRATES.—These salts can be prepared without difficulty in solution, or as hydrates, but the isolation of the anhydrous compounds is not easy: it is accomplished by the action of nitrogen pentoxide on the hydrates.

Cobaltous nitrate, $Co(NO_3)_2$, is, when anhydrous, a pink substance which decomposes at about 100°. The red hexahydrate, $Co(NO_3)_2.6H_2O$, is very soluble in water, and is one of the commonest compounds of cobalt. When gently heated it yields cobalt sesquioxide.

Cobaltic nitrate is unknown, at any rate in the solid state.

Nickelous nitrate, $Ni(NO_3)_2$, is when anhydrous a greenish-yellow substance otherwise resembling cobaltous nitrate. The green hexahydrate, $Ni(NO_3)_2.6H_2O$, is very soluble in water, and resembles cobaltous nitrate hexahydrate, but when gently heated yields (probably) nickel sesquioxide (hydrated).

COMPLEX NITRITES.—Cobalt forms a series of salts called the *cobaltinitrites* in which it is tervalent and present in a complex anion, $Co(NO_2)_6'''$; a few similar compounds of iron and of bivalent nickel have been prepared, but they are of minor importance.

Potassium cobaltinitrite, $K_3Co(NO_2)_6$, is precipitated in the hydrated form when a solution of potassium nitrite is mixed with a well-cooled and faintly acid (acetic acid) solution of a cobaltous salt. Some of the nitrite is consumed in oxidizing the cobalt to the tervalent state. The yellow hydrated salt is insoluble in water and has been used as a pigment; it is sometimes called ' FISCHER'S salt ' after its discoverer. Nickel cannot be oxidized in this way to the tervalent state, and in such solutions forms no insoluble derivative, so this compound provides a method of separating cobalt from nickel. The corresponding salt of sodium is soluble in water, but not the ammonium salt. Many other cobaltinitrites have been prepared.

COMPLEX CYANIDES.—Both cobaltous and nickelous solutions yield with cyanide solutions a precipitate of cobaltous or nickelous cyanide, $Co(CN)_2$ or $Ni(CN)_2$, soluble in excess of cyanide with the formation of complex ions. But whereas the cobaltocyanides contain the violet ion $Co(CN)_6''''$ and recall the ferrocyanides, the nickelocyanides contain the yellow ion $Ni(CN)_4''$ and are not particularly stable; their solutions have the reactions of nickel ions. There is, however, a considerable difference in the relative stability of the two- and three-valent states in the complex

cyanides of cobalt and iron, and it is remarkable that the cobalti-cyanides are much more stable than the cobaltocyanides, whereas with iron the ferrocyanides are rather the stabler. The oxidation potential of the change $Co(CN)_6''' \rightarrow Co(CN)_6''''$ is negative on the hydrogen scale, and if cobaltocyanide solutions are boiled they liberate hydrogen, while in the cold they will absorb oxygen from the air. Many of the cobaltocyanides are insoluble in water, and can be precipitated from salt solutions by the addition of a solution of potassium cobaltocyanide.

Cobalticyanides.—*Potassium cobalticyanide*, $K_3Co(CN)_6$, is obtained in solution by boiling a solution of potassium cobaltocyanide:

$$2Co(CN)_6'''' + 2H_2O = 2Co(CN)_6''' + 2OH' + H_2 \uparrow,$$

or by exposing it to the air, when it absorbs oxygen to form the same product. The cobaltocyanide can be precipitated by alcohol from the solution obtained by adding potassium cyanide to a cobaltous solution until the precipitate of cobaltous cyanide dissolves.

Potassium cobalticyanide can be obtained in yellow crystals by evaporation of its solutions: it is isomorphous with potassium ferricyanide.

Cobalticyanic acid, $H_3Co(CN)_6$, is prepared from potassium cobalticyanide and dilute sulphuric acid. Alcohol precipitates potassium sulphate from this solution, and the concentrated filtrate deposits cobalticyanic acid monohydrate, $H_3Co(CN)_6.H_2O$, from which the water can be expelled by cautious warming. The product is a colourless substance, strongly acid in solution. Numerous cobalticyanides can be prepared.

Since the nickelocyanides are much less stable than the cobalti-cyanides, nickel can be precipitated from mixed cyanide solutions by reagents which leave the cobalt unaffected. LIEBIG's separation of cobalt and nickel depends on the use of bromine water for this purpose. Under suitable conditions it precipitates a hydrated oxide of nickel, probably the sesquioxide, but leaves the cobalti-cyanide unchanged.

CARBONYLS.—Cobalt forms two carbonyls, but they are less easily prepared and more easily decomposed than nickel tetra-carbonyl.

Cobalt tetracarbonyl, $Co_2(CO)_8$, is prepared from cobalt powder (obtained by reducing the oxide in hydrogen) and carbon monoxide at 40 atmospheres pressure and 150°. It is an orange crystalline solid melting at 51°, only slowly attacked by water or moist air. Cryoscopic measurements on the benzene solution lead to a double molecular weight.

Cobalt tricarbonyl, $Co_4(CO)_{12}$, is a black solid prepared by heating

the tetracarbonyl to 60°. On heating, it decomposes into cobalt and carbon monoxide.

Nickel tetracarbonyl, $Ni(CO)_4$, is the only known carbonyl of nickel. It is prepared from reduced nickel and carbon monoxide at about 40°, and in practice it is convenient to work at increased pressure. The product is a colourless liquid freezing at $-25°$ and boiling at 43°; the vapour has the normal molecular weight. Decomposition at atmospheric pressure is complete at 150° or thereabouts, but by raising the pressure it is possible to preserve the carbonyl at much higher temperatures.

Nickel carbonyl is insoluble in water, but slowly liberates hydrogen from acids:

$$Ni(CO)_4 + 2H^{\cdot} = Ni^{\cdot\cdot} + 4CO \uparrow + H_2 \uparrow,$$
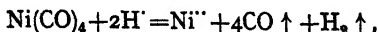
and is decomposed by halogens in the presence of water:

$$Ni(CO)_4 + Cl_2 = NiCl_2 + 4CO \uparrow.$$
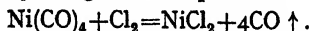
It plays a very important part in the extraction of nickel (p. 799).

Nickel dimethylglyoxime, $Ni(C_4H_7O_2N_2)_2$, appears as a scarlet precipitate when dimethylglyoxime and ammonia are added to the solution of a nickel salt. This is a delicate test for nickel, and the reaction can also be used for the separation of cobalt and nickel, or for the estimation of nickel, as the scarlet substance can be dried and weighed.

RUTHENIUM, RHODIUM, PALLADIUM

Ru=101·1; *atomic number,* 44   Rh=102·91; *atomic number,* 45

Pd=106·4; *atomic number,* 46

These are all rare elements, though palladium is commoner than the other two. Ruthenium was discovered by OSANN in 1828 in minerals from the Ural Mountains, rhodium and palladium in 1804 by WOLLASTON in platinum ores.

Occurrence and Extraction.—*Ruthenium* is obtained from osmiridium, a naturally-occurring alloy of which some samples contain 5 per cent of it or even more. After most of the osmium has been distilled off as the volatile tetroxide (p. 817) the residue is evaporated to dryness with ammonium chloride and a little nitric acid, leaving a solid consisting principally of ammonium hexachloro-iridate, $(NH_4)_2IrCl_6$, but also containing the ruthenium as ammonium hexachloro-ruthenate, $(NH_4)_2RuCl_6$. This is strongly heated, when chlorine and ammonium chloride are expelled, and the finely-divided metals remain. These are heated in a silver crucible with fused caustic potash and potassium nitrate, which convert ruthenium to soluble potassium ruthenate, K_2RuO_4. The product is extracted with water, which dissolves the potassium ruthenate but leaves the

iridium, and the ruthenium is precipitated as oxide by the addition of nitric acid. From this the metal can be obtained by reduction with hydrogen or by various other processes, but the product is not very pure. Traces of osmium may be removed by heating the metal or the oxide in a current of oxygen at such a temperature that osmium volatilizes as the tetroxide, while the ruthenium oxide remains behind, for the volatile ruthenium tetroxide is not produced in these conditions. The ruthenium oxide is reduced to the metal with hydrogen, converted as before to potassium ruthenate, and dissolved in water. A current of chlorine is then passed through the hot solution, converting the ruthenium to volatile ruthenium tetroxide, RuO_4, which distils over and is collected in caustic potash. From this solution pure ruthenium can be obtained by reduction with alcohol.

Rhodium is obtained from the platinum ores of South America (Colombia), the Urals, and British Columbia. When the platinum has been precipitated as ammonium hexachloro-platinate, $(NH_4)_2PtCl_6$ (p. 823), the filtrate is treated with iron, which precipitates rhodium and other metals of the platinum group. The isolation of rhodium from this mixture is a lengthy process which varies according to the metals present; the most effective method depends on the fact that metallic rhodium is insoluble in boiling aqua regia.

Palladium is derived from several sources, though none of them is abundant. The most important is perhaps the residue from the extraction of nickel by the Mond process. Palladium can easily be separated from the other metals of the platinum group as the insoluble palladium iodide, PdI_2. Palladium is also extracted from certain platinum ores and from *porpesite*, a Brazilian alloy of palladium and gold. This is fused with silver and extracted with dilute nitric acid, which leaves the gold unaffected. Palladium itself is insoluble in the dilute acid, but its alloy with silver will dissolve. The silver is easily removed from the solution as silver chloride, and the palladium can be precipitated with zinc. Palladium is purified by adding hydrogen chloride to its ammoniacal solutions; this precipitates the compound $PdCl_2.2NH_3$, insoluble in water but soluble in ammonia.

Metals.—The metals can be precipitated without difficulty from solutions of their salts. They are all hard; *ruthenium* is grey, *rhodium* and *palladium* silver white (compare iron, cobalt, and nickel). The metals can all be obtained in the finely-divided or spongy form by heating the ammonium complex chlorides, and can also be prepared in colloidal solutions of high catalytic activity. The metals are all very resistant to corrosion, though they can be oxidized by heating in oxygen or air, and are also attacked by fluorine

and chlorine. They are resistant to acids; *ruthenium* dissolves only slowly in aqua regia; *rhodium* will not dissolve even in boiling aqua regia, though some of its alloys will; *palladium*, however, dissolves in hot concentrated acids and even in cold concentrated nitric acid.

Uses.—The rarity of these metals prevents any extensive use being made of them. Rhodium has been used in thermo-couples, and, alloyed with platinum, in the manufacture of crucibles, which lose less metal by volatilization at high temperatures than do platinum crucibles. Alloys of palladium and gold have also been used as substitutes for platinum in the manufacture of laboratory apparatus.

THE COMPOUNDS OF RUTHENIUM, RHODIUM, AND PALLADIUM. —Like all the transition elements, these metals display several valencies, and their chemistry is in consequence somewhat involved. For a detailed account the large works of reference should be consulted. As is found with cobalt, and even with iron, the existence of complexes, very numerous with these elements, greatly affects the stability of the valencies. Ruthenium in its behaviour recalls both manganese and iron; its stablest valencies are three and four, but it can also have valencies of two, six, seven, or eight. Like rhodium and palladium, it forms complex salts with the cyanides; these contain the ion $Ru(CN)_6''''$ and are analogous to the ferrocyanides. The complex chloride anions have the formulae $RuCl_5''$ and $RuCl_6'''$, and in the former the metal is tervalent, but ruthenium forms no alums. In rhodium the valency of three seems to be more stable, especially in complexes, than it is in ruthenium; thus the very stable complex cyanide contains the ion $Rh(CN)_6'''$, analogous to the ferricyanides, and unknown with ruthenium; the chloride complexes are $RhCl_5''$ and $RhCl_6'''$ (compare $RuCl_6'''$); and rhodium forms alums, as well as a yellow potassium rhodinitrite, $K_3Rh(NO_2)_6$, insoluble in water, and strongly recalling potassium cobaltinitrite. In addition to this valency of three, rhodium has a valency of four, most clearly shown in the dioxide, and possibly a valency of two.

In palladium, as in nickel, the principal valency is two, but there are less conspicuous valencies of three and four, occurring almost exclusively in complexes. The ion of the palladocyanides is $Pd(CN)_4''$, and the chloropalladite complex is $PdCl_4''$, but $PdCl_6''$ and $PdCl_6''$ are also known. Rhodium and palladium resemble cobalt, and also iridium and platinum, in the variety and stability of their ammine derivatives.

Our account of the compounds of the three elements must be practically confined to the principal oxides and hydroxides and chlorides, but we may first consider the curious behaviour of

palladium with regard to hydrogen. Palladium will absorb large volumes of the gas, and if water is electrolysed with a palladium cathode, considerable quantities of oxygen are set free at the anode before any hydrogen appears at the cathode. The gas can be completely removed by heating the metal in a vacuum. The many researches which have been devoted to the subject have shown that the absorption is not a truly reversible one, and this has made its investigation very difficult. It is now generally believed that definite hydrides are formed, and that these compounds are capable of forming a solid solution in palladium. The permeability of palladium to hydrogen has been made use of in research, and ruthenium and rhodium share this property of absorbing the gas, though to a lower degree.

OXIDES AND HYDROXIDES.—Several oxides of all these elements have been described: we shall deal only with the more important. On account of the rarity and cost of these elements, the chemistry of their compounds has not been investigated so thoroughly as might be wished.

Ruthenium trihydroxide, $Ru(OH)_3$, is a blackish-brown precipitate obtained by the addition of caustic alkalis to solutions of tervalent ruthenium salts. It is oxidized in the air, and can be reduced to the metal by warming in hydrogen at 40°.

Ruthenium dioxide, RuO_2, sublimes when ruthenium is strongly heated in oxygen, and can be obtained in this way from osmiridium. It is, however, less volatile than osmium tetroxide, OsO_4, a fact which is made use of in the separation of these elements. The dioxide is insoluble in acids, but when heated in the air with fused caustic potash it is oxidized to a *ruthenate* (compare manganese):

$$2RuO_2 + 4OH' + O_2 = 2RuO_4'' + 2H_2O \uparrow.$$

The ruthenates contain the ion RuO_4'' and are consequently derived from the unknown ruthenium trioxide, RuO_3, an interesting resemblance with the ferrates. Potassium ruthenate is also prepared by heating ruthenium with caustic potash and potassium nitrate, and dissolves in water to form an orange solution easily oxidized to a green solution which contains a *perruthenate*. The perruthenates contain the ion RuO_4' and correspond with the permanganates, the ruthenates with the manganates.

Ruthenium tetroxide, RuO_4, distils off when a solution of a ruthenate at 90° is oxidized by chlorine:

$$RuO_4'' + Cl_2 = RuO_4 \uparrow + 2Cl'.$$
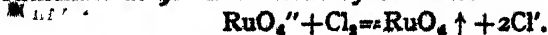
It is a yellow crystalline substance which melts at 26°, and at 106° loses oxygen to form the dioxide. It may be compared with the volatile but more stable tetroxide of osmium. Both of these tetroxides are exceedingly poisonous. It dissolves in water apparently

without producing either an acid or a base (compare osmium tetroxide).

Rhodium trihydroxide, $Rh(OH)_3$, is a yellow compound prepared by the method used for ruthenium trihydroxide; it dissolves in acids to give pink solutions of rhodium salts (compare cobalt).

Rhodium sesquioxide, Rh_2O_3.—This oxide is the sole product of heating the metal, its nitrate, or chloride in air or oxygen at about 600°. It is a grey, crystalline solid, insoluble in acids.

Rhodium dioxide, RhO_2.—The hydrate, $RhO_2.H_2O$ is produced by anodic oxidation of an alkaline solution of the hydroxide, $Rh(OH)_3$.

Rhodates containing the ion RhO_4'' are known, and give blue solutions, but they are much less stable than the ruthenates, and no perrhodates have been prepared.

Palladous oxide, PdO, is a brown or black substance precipitated from palladous solutions by caustic alkalis, or obtained simply by hydrolysing the solution of a palladous salt by boiling it. These methods yield the hydrated substance; the anhydrous oxide can be prepared by igniting palladous nitrate. Palladous oxide is readily reduced by hydrogen in the cold.

Palladium sesquioxide, Pd_2O_3, is obtained by electrolytic oxidation of palladous solutions, but is unstable, and yields a palladous solution (which is further oxidized by electrolysis) and the dioxide.

Palladium dioxide, PdO_2, can be obtained by electrolysis as just described or precipitated from alkaline chloropalladite solutions by ozone:

$$PdCl_4'' + O_3 + 2OH' = PdO_2 \downarrow + O_2 \uparrow + 4Cl' + H_2O.$$
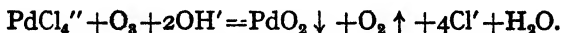
It is an unstable brown substance with oxidizing properties.

HALIDES—**Ruthenium trichloride,** $RuCl_3$, is prepared by the action of hydrochloric acid on the tetroxide or trihydroxide. It dissolves in water to form an orange solution which on heating turns black and deposits the hydroxide (compare ferric chloride).

Chlororuthenites, such as K_2RuCl_5, are prepared from cold concentrated solutions of ruthenium trichloride and other chlorides (e.g. potassium chloride), and *chlororuthenates,* such as K_2RuCl_6, have been prepared by the action of hydrochloric acid on ruthenates, and the hydrate, $RuCl_4.5H_2O$, is known. The chlororuthenates are decomposed by water.

Rhodium trichloride, $RhCl_3$, is obtained by heating ammonium hexachlororhodite, $(NH_4)_3RhCl_6$, when it splits up into ammonium chloride and rhodium trichloride. The anhydrous substance thus obtained is red and will not dissolve in water or acids, but a soluble hydrate can be prepared by the action of hydrochloric acid on rhodium trihydroxide, or by precipitating sodium chloride from

sodium hexachlororhodite, Na_3RhCl_6, with hydrochloric acid and concentrating the solution. Both hexachlororhodites and penta-chlororhodites (which contain the ion $RhCl_5''$) can be obtained from mixed chloride solutions.

Palladous chloride, $PdCl_2$, is obtained by union of the elements, though it is decomposed when heated to 250°, and can be reduced to the metal in the cold by hydrogen. In a current of chlorine it can be distilled at a red heat. It forms dark red crystals, deliques-cent and soluble in water. When mixed with potassium chloride solutions and concentrated, the solutions deposit *potassium chloro-palladite*, K_2PdCl_4, in red crystals which, like palladous chloride, readily decompose on heating. Although no other chloride of palladium is known, complex salts called chloropalladates, in which the metal is quadrivalent, have been prepared. *Potassium chloro-palladate*, K_2PdCl_6, is obtained by passing chlorine through solutions of potassium chloropalladite, and forms red crystals soluble in water, though the solutions are not very stable.

Palladous iodide, PdI_2, is a black substance precipitated from palladous solutions by soluble iodides. As it is insoluble in water it is useful in the separation of palladium from related elements. Like all palladium salts it yields the metal on strong heating. The insolubility of the iodide is one of the resemblances between the adjacent elements palladium and silver. Since the standard elec-trode potential of palladium, $+0·82$ volt, like that of silver ($+0·80$ volt), exceeds that of iodine, which is only $+0·53$ volt, it would not be possible for palladous iodide to exist in solution except in very low concentration.

Palladium trifluoride, PdF_3, can be prepared, by exposing palla-dium, or palladous chloride, to the action of fluorine.

OSMIUM AND IRIDIUM

$Os = 190·2$; *atomic number,* 76 $Ir = 192·2$; *atomic number,* 77

Occurrence and Extraction.—These rare elements were discovered by TENNANT in 1804. The principal source is *osmiridium,* an alloy found in Colombia (South America), the Ural Mountains, and New South Wales, and containing from 20 per cent to 40 per cent of osmium, with most of the rest iridium, and small quantities of ruthenium, rhodium, and platinum.

The osmiridium is first heated with zinc, with which osmium forms an alloy, and the product cooled and crushed. It is then placed in an earthenware crucible and strongly heated with a mixture of barium peroxide and barium nitrate; this treatment brings all the metals present into solution. The product is dissolved in dilute

hydrochloric acid, and sulphuric acid is added to precipitate the barium as sulphate. This is filtered off, and the filtrate is treated with nitric acid to oxidize to the tetroxide, OsO_4, any osmium which may be in a lower state of oxidation. The solution is now boiled, when nearly all the osmium distils off as the volatile tetroxide. The iridium and any ruthenium which may be present remain in the solution, and are obtained in the metallic state as described under ruthenium (p. 809). When these metals are heated with caustic potash and potassium nitrate, a potassium iridate is probably formed as well as a ruthenate, but the subsequent washings decompose the iridate, leaving hydrated iridium dioxide (compare ruthenium and rhodium). This can be converted to the metal by reduction with hydrogen, or simply by heating to a high temperature. As the product contains traces of the other platinum metals it is usually further purified by taking advantage of the insolubility of iridium in fuming nitric acid or in aqua regia. This process will not eliminate the closely allied element rhodium, but rhodium will dissolve in fused potassium hydrogen sulphate, which converts iridium to the insoluble sesquioxide, Ir_2O_3.

The volatile osmium tetroxide obtained as just described is redistilled and collected in aqueous ammonia, then precipitated from this solution by hydrogen sulphide as osmium tetrasulphide, OsS_4. When heated in the absence of air this substance dissociates: the sulphur volatilizes first, and then the osmium sublimes and can be collected. A very high temperature is required for this operation.

Metals.—Osmium and iridium are easily prepared by reduction of their compounds, in solution or in the solid state. They are white metals, very dense and hard; osmium is the densest of all substances known on the earth (density up to 24). They can be obtained in colloidal solution or in the finely-divided state, and are then very active catalysts for various reactions, such as the decomposition of hydrogen peroxide. Finely-divided osmium is for certain reactions an even more active catalyst than platinum, and has been used in the synthesis of ammonia, though cheaper catalysts have now taken its place.

The metals are oxidized when strongly heated in the air, but they are more resistant than ruthenium or rhodium to the action of fluorine or chlorine. Osmium is readily soluble in fuming nitric acid, but iridium is insoluble in all acids. In spite of their exceptional properties, the elements are too expensive to be of much practical use. Osmium was once used for the filaments of electric-light bulbs, but has long been replaced by the cheaper tungsten. Alloys of platinum and iridium are hard and incorrodible, and have been used in tipping the nibs of expensive fountain pens, in surgical instruments, and in the construction of the standard metre and

kilogram at Paris.   Platinum crucibles often contain a little iridium to stiffen them.

THE COMPOUNDS OF OSMIUM AND IRIDIUM.—The principal valencies of osmium are four, six, and eight, but there is a well-marked valency of three, especially noticeable in complex anions. Osmium tetroxide, OsO_4, in which the metal is octavalent, is more stable than the corresponding compound of ruthenium, and osmium is the only element to form, in the octafluoride OsF_8, an electrically neutral compound in which so many as eight atoms of one element are directly attached to one atom of another.   In its complex chlorides osmium resembles ruthenium in displaying valencies of three and four: three in the chloro-osmites, $OsCl_6'''$, and four in the chloro-osmates, $OsCl_6''$, and it also resembles ruthenium in forming osmocyanides, $Os(CN)_6''''$, in which the metal is bivalent; potassium ferrocyanide, ruthenocyanide, and osmocyanide are isomorphous. Iridium, as might be expected, shows a close resemblance to rhodium as well as to osmium.   The valency of three is well marked and fairly stable, though the hydrated sesquioxide, Ir_2O_3, is oxidized by the air.   Iridium forms alums, and also a sulphate, $Ir_2(SO_4)_3.Aq.$, in which it is tervalent.   Moreover, the only known complex cyanides are the iridicyanides, $Ir(CN)_6'''$, as with rhodium, though in its complex chlorides iridium resembles osmium rather than rhodium, forming the chloroiridites, $IrCl_6'''$, and the chloro-iridates, $IrCl_6''$.   The valency of four is less stable with iridium than with osmium, the valency of six is very unstable, and higher valencies are unknown.   Like cobalt and rhodium, iridium very readily forms complex ammines.   The known compounds of sexivalent iridium comprise the fluoride, IrF_6, the trioxide, IrO_3, and possibly an oxyfluoride, $IrOF_4$.   All are powerful oxidizing agents. The hexafluoride, obtained from the metal and fluorine at 260°, is violently attacked by water, yielding finally the tetrahydroxide, $Ir(OH)_4$, with hydrogen fluoride.

OXIDES AND HYDROXIDES.—The most important are the following:

Osmium tetrahydroxide, $Os(OH)_4$, is precipitated when chloro-osmate solutions are boiled with caustic alkalis in the absence of air:

$$OsCl_6'' + 4OH' = Os(OH)_4 \downarrow + 6Cl'.$$
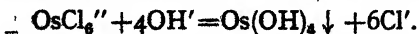
It is oxidized by the air to the tetroxide, OsO_4.   If the tetrahydroxide is heated in an inert atmosphere it loses water and forms the dioxide, OsO_2, which can also be prepared by gently heating osmium in a stream of osmium tetroxide vapour.   The dioxide is a brown solid which on strong heating yields osmium and the volatile tetroxide:

$$2OsO_2 = Os + OsO_4 \uparrow.$$
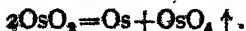
With hydrochloric acid it yields the complex $OsCl_6''$.

Osmium tetroxide, OsO_4.—Solutions of this substance are often called 'osmic acid,' and salts such as $K_2OsO_4(OH)_2$ have been obtained by treating the tetroxide with concentrated alkalis, but such salts are *perosmates*. Osmium tetroxide concludes a series—TaO_4''', WO_4'', ReO_4', OsO_4—in which the charge is the difference (8—group number), and in all of which the four oxygen atoms are found at the corners of a regular tetrahedron enclosing the characteristic atom at its centre.

This oxide is produced by heating the metal or its compounds in oxygen, or by treating them with nitric acid. It is a colourless solid with remarkable properties, for it melts at 40° and boils at 130°, and has so high a vapour pressure at temperatures below the boiling-point that it can be distilled without difficulty from its aqueous solutions. The vapour, which has the normal vapour density, has a strong peculiar odour, and is highly poisonous, causing temporary blindness, among other effects. It is an oxidizing agent and can easily be reduced to the metal, either in solution or in the vapour. A dilute solution is used as a stain in microscopy, since organic substances reduce it to black finely-divided osmium. It also forms a useful killing agent for protozoa, etc. Solutions of osmium tetroxide are neutral.

Osmates and Osmyl Compounds.—The trioxide is unknown, but osmates, derived from an acid, H_2OsO_4, have been prepared (compare iron and ruthenium). They are conveniently obtained by reducing alkaline solutions of osmium tetroxide, e.g. with alcohol. On careful treatment with acids, osmate solutions yield a series of derivatives of a type infrequently seen. They are called *osmyl compounds*, and contain the bivalent positive radical OsO_2, or possibly the ion $OsO_2{\cdot\cdot}$, always associated, however, with other ions to produce compounds of the type $K_2(OsO_2)Cl_4$, potassium osmyl chloride. Their formation from osmates may be formulated:

$$OsO_4'' + 4H{\cdot} \rightleftharpoons OsO_2{\cdot\cdot} + 2H_2O,$$
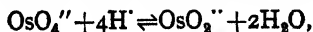
and is reversible, for in neutral solution the osmyl derivatives are hydrolysed and precipitate what may be osmic acid, H_2OsO_4. They are, however, stable in slightly acid solution.

Iridium sesquioxide, Ir_2O_3, is obtained by heating chloroiridates, M_2IrCl_6, with sodium carbonate, when oxygen as well as carbon dioxide escapes.

Iridium tetrahydroxide, $Ir(OH)_4$, and **dioxide,** IrO_2, are prepared by the method used for the corresponding osmium compounds, but when the dioxide is strongly heated, it yields iridium and oxygen, since iridium forms no tetroxide. The hydroxide is a blue-black, and the dioxide a black, powder. The latter has a crystal structure similar to that of manganese dioxide (p. 763).

HALIDES.—Osmium reacts with fluorine when heated in a stream of the gas, and forms a tetrafluoride OsF_4, a hexafluoride OsF_6, and an octafluoride OsF_8, which can be separated by fractional distillation *in vacuo.*

Osmium octafluoride, the most volatile of the three, is a yellowish-red solid melting at 35°, and boiling at 48° to form a colourless vapour which fumes in moist air and has the normal vapour density. The octafluoride dissolves in water and the solution is partially hydrolysed, with formation of the tetroxide. It is decomposed by heating and is highly reactive, attacking organic substances with violence. It apparently combines with fluorides of the alkali-metals to form double or complex fluorides, and this may indicate a covalency of more than eight for osmium.

Osmium dichloride, $OsCl_2$, has been prepared by heating the trichloride under reduced pressure.

Osmium trichloride, $OsCl_3$, is prepared by heating ammonium chloro-osmate, $(NH_4)_2OsCl_6$, in chlorine. It is a brown solid which dissolves in water to form solutions which, though slightly hydrolysed, are stable in the air. The *chloro-osmites*, such as K_3OsCl_6, potassium chloro-osmite, are derived from it, and form red solutions: the potassium and ammonium salts, and possibly others as well, are soluble in water.

Osmium tetrachloride, $OsCl_4$, is prepared by union of the elements at a high temperature, and when purified by sublimation forms a black solid. As it is insoluble in water, the *chloro-osmates*, which contain the ion $OsCl_6''$, cannot be prepared from its solutions, but they can be made by other methods, e.g. by heating osmium and potassium chloride in chlorine. Their solutions, which are yellow, are hydrolysed on warming and precipitate the tetrahydroxide.

Iridium dichloride, $IrCl_2$, is prepared by heating the trichloride in a stream of chlorine at 600°–700°. Above 770° the dichloride dissociates to give the copper-red monochloride, IrCl.

Iridium trichloride, $IrCl_3$, prepared like the osmium compound, is a green solid insoluble in water, but a soluble hydrated variety has been prepared (compare rhodium trichloride). The *chloro-iridites*, with the ion $IrCl_6'''$, form green solutions and resemble the osmium compounds.

Iridium tetrachloride, $IrCl_4$, is prepared by union of the elements like osmium tetrachloride, but as it readily forms the trichloride the chlorine must be introduced under pressure. It differs from the osmium compound in being soluble in water and less stable The *chloroiridates*, such as potassium chloroiridate, K_2IrCl_6, are derived from it, and can be made either in solution or by the method used for the chloro-osmates, but the potassium and ammonium salts are less soluble in water than the corresponding osmium compounds, and

the chloroiridates lose chlorine when their solutions are boiled, becoming chloroiridites, whereas chloro-osmates are merely hydrolysed.

Iridium trisulphate.—$Ir_2(SO_4)_3$, can be obtained as a hydrate from a solution of the sesquioxide in sulphuric acid. It is soluble in water to give a bright yellow solution which is oxidized and turned violet by the air, but if a concentrated solution is evaporated with potassium sulphate solution, *potassium iridium alum*, K_2SO_4, $Ir_2(SO_4)_3.24H_2O$, can be obtained. Osmium forms neither a trisulphate nor an alum.

PLATINUM

$Pt=195.09$. *Atomic Number*, 78

Platinum was discovered in South America, in a district which now forms part of Colombia. It was first brought to Europe in 1735

Occurrence and Extraction.—Platinum occurs in the Ural Mountains in the form of an alloy containing some 80 per cent of platinum together with iron, copper, the other metals of the platinum group, and sometimes a little gold. There are also deposits containing platinum sulphide in the Transvaal, though they are not worked at present. The most important source of platinum is now, however, the residue of the extraction of nickel from the Ontario ores (p. 799).

Crude platinum from all these sources is brought into solution with aqua regia, and the solution is diluted, filtered, and evaporated to small bulk. Nitric acid is then expelled by boiling with hydrochloric acid, and the chlorides are evaporated to dryness and then dissolved in a little water. The addition of ammonium chloride precipitates the slightly soluble ammonium chloroplatinate, $(NH_4)_2PtCl_6$, with some ammonium chloroiridate, $(NH_4)_2IrCl_6$. These are filtered off, and the mother-liquors are worked up again. The precipitate is suspended in water and sulphur dioxide bubbled through, when soluble ammonium chloroiridite, $(NH_4)_3IrCl_6$, is formed by reduction, and only the ammonium chloroplatinate, which is not so easily reduced, remains undissolved. Heating converts it to spongy platinum, which is welded into an ingot in a lime furnace heated either electrically or in the oxy-hydrogen flame.

Metallic Platinum.—Platinum is a very dense silver-white metal. It is not so hard as osmium or iridium, but it is more malleable and ductile, and can be drawn into thin strong wires. Its coefficient of thermal expansion is about 9×10^{-6}, and is very close to that of glass, so that before the discovery of cheaper substitutes platinum was much used for sealing into glass; the possibility of doing this is still a great convenience in the manufacture of apparatus which for other reasons must contain platinum.

The metal is very resistant to oxygen even at high temperatures, though the slight loss in weight which platinum articles suffer when strongly heated for a long time in the air, but not in inert gases, has been attributed to the formation of the dioxide PtO_2. With few exceptions, acids have no effect on the metal, but boiling concentrated sulphuric acid attacks it slightly, while aqua regia, and a solution of a chlorate in concentrated hydrochloric acid, dissolve it without difficulty. Their solvent action is due to the liberation of chlorine, though massive platinum is not attacked by chlorine, nor even by fluorine, up to a temperature of more than 350°. The fused hydroxide, nitrate and bisulphate of potassium, and sodium peroxide, attack platinum, and crucibles made from it should not be used for strongly heating these substances, nor is it prudent to melt metals in platinum crucibles, as alloying frequently takes place. Contact with hot elementary sulphur or phosphorus should also be avoided, and direct heating with a coal-gas flame may lead to action with the sulphur compounds present in the gas.

Its resistance to chemical attack and its high melting-point make platinum almost indispensable to the manufacture of certain kinds of apparatus, though its cost, which in the last twenty years has fluctuated widely, is a serious disadvantage. It is used for crucibles and basins and other chemical ware, for wires for flame tests, for electrical contacts, for electrodes, in pyrometers, resistance thermometers, electric furnaces, standard weights and measures, and for many other purposes. Platinum and platinum-iridium have often been used to make vessels to hold hydrofluoric acid or fluorine. The cost of platinum is generally so high that the use of substitutes has become absolutely necessary. Crucibles can be made from nickel, silver, gold, fused silica, alumina, or zirconia, according to the purpose for which they are required; platinum wires for analysis can be replaced by fused silica; ' platinite ' (p. 800) can be used for sealing into glass, and fluorine or hydrofluoric acid apparatus is made from modern ' plastics ' or copper, while weights can be plated with platinum or with gold.

Platinum is also greatly in demand as a catalyst. A hot platinum wire will continue to glow in a mixture of methyl alcohol vapour and air, formaldehyde being formed on the surface of the metal, or in coal-gas and air, and will ignite a jet of hydrogen. Colloidal platinum, prepared by BREDIG's method or by careful reduction, is a very active catalyst excelled only, in certain reactions, by colloidal osmium. On the industrial scale platinized asbestos is often employed; this is prepared by soaking asbestos in a solution of chloroplatinic acid and then producing the finely-divided metal by reduction. Vigorous reduction of solutions of platinum salts produces another finely-divided modification called ' platinum

black,' often used for coating the platinum electrodes of delicate apparatus such as hydrogen electrodes or conductivity cells. On the other hand, the use of smooth platinum anodes is essential to certain anodic oxidation processes, such as the manufacture of persulphates, in which a high oxygen over-voltage is required.

Quite large quantities of platinum were at one time used in the oxidation of sulphur dioxide (p. 684), but cheaper catalysts are now employed. On the other hand, grids of platinum wire are still used in the oxidation of ammonia to nitric acid (p. 390).

Platinum is also used in jewelry—a waste of valuable material that ought not to be encouraged.

COMPOUNDS OF PLATINUM.—The principal valencies of platinum are two and four, but it may possibly show an unstable valency of three, and more rarely a valency of six. The covalency or co-ordination number is usually four when the metal is bivalent, and six when it is quadrivalent.

Platinum is one of the least electropositive of metals, and the negligible tendency of the metal to form ions in contact with water is the reason for the use of platinum in electrometric apparatus. It shows the greatest reluctance to form cations: the bivalent compounds are either insoluble or contain the metal in the anion, and the quadrivalent compounds react with water to form complexes of the same nature (see, for example, platinic chloride).

The chemistry of platinum solutions is therefore chiefly the chemistry of its complexes. In the chloroplatinates, with the ion $PtCl_6''$, the quadrivalent state absent in nickel and inconspicuous in palladium is now very stable. On the other hand no quadrivalent complex cyanides are known, and the platinocyanides, $Pt(CN)_4''$, corresponding with the palladocyanides and nickelocyanides, are exceedingly stable compounds. Just as nickel resembles the adjacent element copper, and palladium silver, so does platinum resemble gold.

Like other members of the group, platinum forms a large range of complex ammines, some of which have already been alluded to (pp. 201, 349, 350).

OXIDES.—The principal oxides of platinum are the monoxide, dioxide, and trioxide. They all yield the metal and oxygen on strong heating.

Platinum monoxide, PtO, is prepared by the action of oxygen on platinum sponge at 450°. In the hydrated condition it can be precipitated by boiling a chloroplatinite with caustic soda:

$$PtCl_4''+2OH'\rightarrow PtO.Aq. \downarrow +4Cl'+H_2O.$$

It is a reducing agent, oxidized by the air, and if prepared in the wet way cannot be freed from water without decomposition.

Platinum dioxide, PtO_2, is precipitated as a hydrate when a solution of platinic chloride which has been boiled with caustic alkali is treated with a weak acid—acetic acid. The white precipitate is soluble in acids and alkalis, and probably has the constitution $H_2Pt(OH)_6$, since from its alkaline solutions such salts as *potassium hexahydroxyplatinate*, $K_2Pt(OH)_6$, can be obtained, and behave as the salts of a strong acid.

Platinum trioxide, PtO_3.—By anodic oxidation of potassium hexahydroxyplatinate solutions, *potassium platinate*, K_2PtO_4, is obtained, and when treated with acids this yields the trioxide as a red solid. It is a powerful oxidizing agent which gives off oxygen when gently warmed.

· HALIDES.—Platinum forms stable halides in which it is bivalent and quadrivalent, and a less stable tervalent series. All the halides decompose into the elements on ignition. The bivalent halides are insoluble in water. The quadrivalent halides (except the iodide) dissolve, but they react with the water to form complexes in which the platinum is in the anion; their solutions have consequently an acid reaction. Complexes such as $PtCl_4''$ and $PtCl_6''$ are very stable and are the anions of strong acids. The trihalides behave towards water like mixtures of the dihalides and tetrahalides. The tetrahalides are weak oxidizing agents, and their oxidizing action is assisted by the insolubility of the dihalides (compare copper).

The **Fluorides** must be prepared by union of the elements at 500°–600°: *platinous fluoride*, PtF_2, is insoluble in water; *platinic fluoride*, PtF_4, is soluble but easily hydrolysed.

Platinous chloride, $PtCl_2$, is made by union of the elements at 360°, and is insoluble in water, but dissolves readily in chloride solutions to form a series of salts called the *chloroplatinites*, with the ion $PtCl_4''$. These compounds can also be prepared by reducing chloroplatinate solutions, as for instance with sulphur dioxide. The silver, mercury, and lead salts are insoluble, the others mostly soluble, the solutions being red. The chloroplatinite solutions are fairly stable, but they are decomposed by boiling caustic alkali or by hydrogen sulphide, and oxidized to chloroplatinates by chlorine. · ·

Platinum trichloride, $PtCl_3$, is made by heating the tetrachloride in chlorine at 390°. It is soluble in boiling water, but the solution is easily hydrolysed. With chloride solutions it gives a mixture of chloroplatinite and chloroplatinate.

Platinum tetrachloride, Platinic chloride, $PtCl_4$, is made by heating chloroplatinic acid, H_2PtCl_6, in chlorine. It is a reddish-brown hygroscopic solid soluble in water to form a stable solution from which the hydrate $PtCl_4.H_2O$ can be obtained by evaporation

hydrolysis takes place on further heating. The solution has an acid reaction, and is dibasic, as is shown by titration: on electrolysis the platinum travels towards the anode. The solution is therefore supposed to contain the acid $H_2PtCl_4(OH)_2$, with the anion $PtCl_4(OH)_2''$—compare hexahydroxyplatinic acid, $H_2Pt(OH)_6$.

Chloroplatinic acid, H_2PtCl_6, is obtained in solution by dissolving platinum tetrachloride in hydrochloric acid, or by dissolving platinum in aqua regia, evaporating repeatedly to dryness with hydrochloric acid, and treating the final aqueous solution with chlorine. The hexahydrate, $H_2PtCl_6.6H_2O$, is obtained by concentration of its solutions. It is a strong acid and yields salts on neutralization with alkalis; these salts can also be obtained by oxidizing the chloroplatinites with chlorine. Their solutions are yellow.

Potassium chloroplatinate, K_2PtCl_6, like the chloroplatinates of rubidium, caesium, ammonium, and silver, is a yellow salt only slightly soluble in cold water (about 9 gm. per litre at room temperature), so it can be obtained by precipitation. It was formerly used in the quantitative analysis of potassium salts, but is now often replaced by the cheaper potassium perchlorate. On strong heating it leaves potassium chloride and platinum.

The **Bromides** resemble the chlorides, but the *bromoplatinates* of potassium and ammonium are more soluble than the corresponding compounds of chlorine.

Platinic iodide, PtI_4, is an insoluble compound prepared by·union of the elements, or precipitated by iodides from chloroplatinate solutions. It loses iodine *in vacuo* even at room temperature. *Potassium iodoplatinate*, K_2PtI_6, is soluble in water.

SULPHIDES.—**Platinous sulphide,** PtS, and **platinic sulphide,** PtS_2, are precipitated by hydrogen sulphide from chloroplatinite and chloroplatinate solutions respectively. They decompose into the elements when heated in the absence of air.

Platinic sulphate, $Pt(SO_4)_2$, is deposited as the tetrahydrate when a current is passed between platinum electrodes in fairly concentrated sulphuric acid. It is soluble in water, but precipitates a basic salt on warming.

Complex cyanides.—The *platinocyanides*, with the ion $Pt(CN)_4''$, are more important and more stable than the *platinicyanides*, with the ion $Pt(CN)_4'$: it should be noted that the latter contain tervalent, not quadrivalent, platinum. The former are obtained by the addition of cyanides to most platinous or platinic solutions, e.g. with platinic chloride:

$$PtCl_4+6CN'=Pt(CN)_4''+4Cl'+C_2N_2\uparrow,$$

a reaction that may be compared with the action of cyanides on
D

copper solutions. The platinocyanides are very stable compounds unaffected by aqua regia. Many of them are beautifully coloured, as for example the ammonium salt, which appears pink, blue, or yellow according to the direction of the incident light. Many fluoresce in ultra-violet light or when exposed to the rays from radioactive substances.

Barium platinocyanide, $BaPt(CN)_4.4H_2O$, prepared from platinous chloride and barium cyanide solution, fluoresces very brilliantly under X-radiation, and is much used in screens for radiographic investigations.

LIST OF THE ELEMENTS

In Alphabetical Order

Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	(227)
Aluminium	Al	13	26·98
Antimony	Sb	51	121·76
Argon	A	18	39·944
Arsenic	As	33	74·91
Barium	Ba	56	137·36
Beryllium	Be	4	9·013
Bismuth	Bi	83	209·00
Boron	B	5	10·82
Bromine	Br	35	79·916
Cadmium	Cd	48	112·41
Caesium	Cs	55	132·91
Calcium	Ca	20	40·08
Carbon	C	6	12·011
Cerium	Ce	58	140·13
Chlorine	Cl	17	35·457
Chromium	Cr	24	52·01
Cobalt	Co	27	58·94
Copper	Cu	29	63·54
Dysprosium	Dy	66	162·51
Erbium	Er	68	167·27
Europium	Eu	63	152·0
Fluorine	F	9	19·00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157·26
Gallium	Ga	31	69·72
Germanium	Ge	32	72·60
Gold	Au	79	197·0
Hafnium	Hf	72	178·5
Helium	He	2	4·003

Element	Symbol	Atomic Number	Atomic Weight
Holmium	Ho	67	164·94
Hydrogen	H	1	1·0080
Indium	In	49	114·82
Iodine	I	53	126·91
Iridium	Ir	77	192·2
Iron	Fe	26	55·85
Krypton	Kr	36	83·80
Lanthanum	La ·	57	138·92
Lead	Pb	82	207·21
Lithium	Li	3	6·940
Lutetium	Lu	71	179·99
Magnesium	Mg	12	24·32
Manganese	Mn	25	54·94
Mercury	Hg	80	200·61
Molybdenum	Mo	42	95·95
Neodymium	Nd	60	144·27
Neon	Ne	10	20·183
Nickel	Ni	28	58·71
Niobium	Nb	41	92·91
Nitrogen	N	7	14·008
Osmium	Os	76	190·2
Oxygen	O	**8**	**16·00**
Palladium	Pd	46	106·4
Phosphorus	P	15	30·975
Platinum	Pt	78	195·09
Polonium	Po	84	210
Potassium	K	19	39·100
Praseodymium	Pr	59	140·92
Proto-actinium	Pa	91	(231)
Radium	Ra	88—	225·97
Radon	Rn	86	(222)
Rhenium	Re	75	186·22
Rhodium	Rh	45	102·91
Rubidium	Rb	37	85·48
Ruthenium	Ru	44	101·1
Samarium	Sm	62	150·35

Element	Symbol	Atomic Number	Atomic Weight
Scandium	Sc	21	44·96
Selenium	Se	34	78·96
Silicon	Si	14	28·09
Silver	Ag	47	107·880
Sodium	Na	11	22·991
Strontium	Sr	38	87·63
Sulphur	S	16	32·066
Tantalum	Ta	73	180·95
Technetium	Tc	43	(99)
Tellurium	Te	52	127·61
Terbium	Tb	65	158·93
Thallium	Tl	81	204·39
Thorium	Th	90	232·05
Thulium	Tm	69	168·94
Tin	Sn	50	118·70
Titanium	Ti	22	47·90
Tungsten	W	74	183·86
Uranium	U	92	238·07
Vanadium	V	23	50·95
Xenon	Xe	54	131·30
Ytterbium	Yb	70	173·04
Yttrium	Y	39.	88·92
Zinc	Zn	30	65·38
Zirconium	Zr	40	91·22

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